

# 9th International Conference on Surface and Colloid Science



## BOOK OF ABSTRACTS

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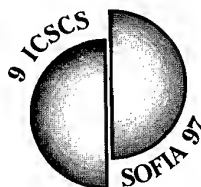
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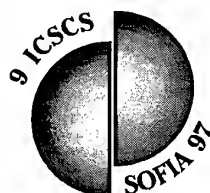
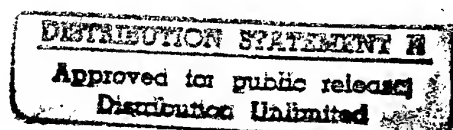
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6-12 July, 1997, Sofia, Bulgaria

# BOOK OF ABSTRACTS

**9th International Conference on Surface  
and Colloid Science,  
6 - 12 July, 1997, Sofia, Bulgaria**



**Sofia, 1997**

**Issued by the Organizing Committee of 9ICSCS**

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## *Preface*

This volume collects the abstracts of the papers submitted (before Easter 1997) at the Ninth International Conference on Surface and Colloid Science (9ICSCS), Sofia, 6 - 12 July 1997. The conference seems to be the greatest worldwide forum in this scientific field and it is organized every three years under the auspices of the International Association of Colloid and Interface Scientists (IACIS).

Authors from 50 countries from all over the world have submitted abstracts of papers for presentation at the conference. Almost 1000 papers are distributed in sections according with 10 Focus Areas that include 45 Topics (see the Table). Most of the papers are included as Keynote Lectures, Oral Presentations and Posters in several sessions of the Conference Program (some of the papers are not in the program since their authors cannot attend the conference).

All the abstracts are numbered from 1 to 959. In any code the capital letter refers to the corresponding Focus Area and the last figure is the Topic of that Focus Area. In each Topic the abstracts are located in alphabetic order of the family name of the first author.

Also, at the very beginning, the abstracts of six plenary lectures are presented. These abstracts are marked by Roman numerals.

We believe that such a great variety of papers provides a well-balanced perspective of the current research over the entire field together with indicating some important open questions.

*B.V. Toshev*

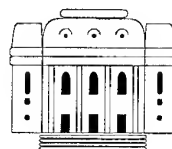


# *9th International Conference on Surface and Colloid Science*

organized by the



*Bulgarian Academy of Sciences,  
Institute of Physical Chemistry*



*University of Sofia,  
Department of Physical Chemistry*

under the auspices of the



*International Association of Colloid and Interface Scientists*

The 9th International Conference on Surface and Colloid Science (9ICSCS) is a succession from the series of the greatest worldwide forums in this scientific field organized under the auspices of the International Association of Colloid and Interface Scientists (IACIS) every three years. Eight conferences have been successfully held so far: Budapest, Hungary (1975), Puerto Rico (1976), Stockholm, Sweden (1979), Jerusalem, Israel (1981), Potsdam NY, USA (1985), Hakone, Japan (1988), Compiègne, France (1991), and Adelaide, Australia (1994). The 10th ICSCS is scheduled for the year 2000 in Bristol, United Kingdom.

The 9ICSCS is held from Sunday, July 6 to Saturday July 12, 1997, at the National Palace of Culture - Congress Center located in the central part of Sofia, Bulgaria. It gathers scientists from both academic and industrial laboratories and covers the most important and fast developing branches of the colloid and interface science.

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*The Organizing Committee of 9ICSCS acknowledges with many thanks the financial support of the sponsors whose generous contributions made possible the realization of the conference!*

	Focus Areas	Topics
<b>A</b>	<b>Colloidal Dispersions</b>	A1 Suspensions A2 Concentrated Dispersions A3 Foams A4 Emulsions A5 Nanoparticles A6 Complex Dispersions A7 Aerocolloidal Systems
<b>B</b>	<b>Capillarity</b>	B1 Surface Thermodynamics B2 Thin Liquid Films B3 Monolayers and Multilayers B4 Wetting and Adhesion B5 Contact Angles and Surface Modification B6 Nucleation
<b>C</b>	<b>Colloid Stability</b>	C1 Surface Forces C2 Thin Films, including Bilayers C3 Dissolution of Concentrated Colloidal Systems
<b>D</b>	<b>Self-Assembled Matter</b>	D1 Self-Assembly in Amphiphilic Systems D2 Structural Stability D3 Vesicles D4 Microemulsions D5 Gels
<b>E</b>	<b>Surfactants and Polymers</b>	E1 Surfactants in Solution E2 Surfactants at Interfaces E3 Polymers in Solution E4 Polymers at Interfaces E5 Polymer/Surfactant Interactions
<b>F</b>	<b>Charged Particles and Interfaces</b>	F1 Electric Surface Phenomena F2 Electro-Optical Phenomena F3 Dielectric Phenomena
<b>G</b>	<b>Dynamics of Interfaces and Colloids</b>	G1 Dynamic Properties of Interfaces G2 Dynamics of Monolayers G3 Rheology G4 Physico-Chemical Mechanics
<b>H</b>	<b>Biocolloids and Biointerfaces</b>	H1 Biomembranes H2 Colloidal Aspects of Cell Functions H3 Biosurfactants and Biomaterials H4 Colloids and Surfactants in Medicine H5 Drug Delivery
<b>K</b>	<b>Technological Applications</b>	K1 Colloids and Surfactants in Pharmacy and Cosmetics K2 Food Colloids K3 Colloids in Oil Production K4 Mineral Processing / Flotation
<b>L</b>	<b>Environmental Colloid Science</b>	L1 Water Pollution and Treatment L2 Air Pollution: Aerosols L3 Agricultural Colloid Science

# Plenary Lectures

## **I. ION BINDING AND ION SPECIFICITY: THE HOFMEISTER EFFECT, ONSAGER AND LIFSHITZ THEORIES**

**Barry W. Ninham**

*Department of Applied Mathematics, Research School of Physical Sciences and Engineering, Institute of Advanced Studies, Australian National University, Canberra, Australia 0200*

Present theories of colloid science do not account for specific ion effects as exemplified by the Hofmeister effect, surface tension of electrolyte solutions, binding to micelles, effective charge in double layer interactions, and attractive interactions in low Hamaker constant systems. It is argued that specificity emerges naturally and can be rationalised if dispersion interactions acting on ions are included in the theory. These are in principle accessible from bulk solution properties. Specific ion adsorption due to dispersion interactions can be dominant even at charged interfaces especially at high salt concentrations ( $> 0.1\text{M}$ ). The effects can be qualitatively different at air-water and at oil-water interfaces. That part of extended Lifshitz theory for low Hamaker constant systems, in which the forces are mainly due to temperature and salt dependent interactions, is reexamined. It is shown to be at the same level of approximations, and precisely equivalent to the Onsager limiting law for the interfacial tension change due to dissolved salt at a single interface., i.e., to linearisation of the Poisson Boltzmann distribution, and restriction to electrostatic potentials as the determinant of adsorption excesses. The usual description of interactions into separate electrostatic and dispersion interactions is invalid, even at the level of continuum (primitive model) theories.

## **II. SELF-ASSEMBLY OF SMALL AND LARGE AMPHIPHILES: BULK BEHAVIOUR AND THE EFFECT OF POLYMERS AND SURFACES**

**B. Lindman, P. Alexandridis, U. Olsson, L. Piculell, F. Tiberg and K. Thuresson**

*Physical Chemistry 1, Chemical Center, Lund University, P O B 124, S-221 00, Lund, Sweden*

Amphiphilic polymers are interesting alternatives to surfactants. After reviewing different types of amphiphilic copolymers we consider their self-assembly and compare it to that of simple surfactants. Self-assembly varies strongly with copolymer architecture but for block copolymers there is a close resemblance to surfactant behaviour. However, as described by phase diagrams for ternary polymer-oil-water systems, the variation in self-assembly structure is much richer for copolymers; the richness increases with copolymer molecular weight.

Surfactant self-assembly may be strongly influenced by the presence of polymer molecules, the effect depending strongly on the character of the polymer. Surfactant adsorption at solid surfaces is also generally best considered as a self-assembly process influenced by the presence of the interface. The presentation will review some recent results pertaining to surfactant self-assembly in polymer solutions and at solid surfaces and compare those with the behaviour of simple surfactant solutions. Adsorption can lead to continuous layers or discrete aggregates on the surface depending on the balance between the polar head and the alkyl chain.

For polymer-surfactant mixtures, attractive or repulsive interactions are observed depending on the system. Different types of phase separation phenomena are encountered including segregative and associative types. It is found fruitful to analyse the phase diagrams of polymer-surfactant systems with those of polymer-polymer and surfactant-surfactant mixtures as a basis. Analogies and differences are discussed and it is found that polymer-surfactant systems show basic similarities to polymer-polymer systems, while surfactant mixtures are different, which is due to the formation of mixed micelles.

Different types of surfactant systems are compared and it is found that in all cases surfactant aggregates may have different sizes and structures depending on the conditions and that there is a close correspondence between the different situations. As an example, surfactant self-assemblies of nonionic surfactants are continuous for shorter ethylene oxide chains but discrete micellar for larger polar head-groups.

### **III. BIG ENOUGH AND SMALL ENOUGH – COLLOID AND SURFACE FORCES ON SINGLE BIOLOGICAL MACROMOLECULES**

**V. Adrian Parsegian**

*National Institutes of Health, Bethesda, MD 20892-5626, USA*

Between the "small" of ordinary molecules and the "large" of colloids, biological macromolecules are simultaneously microscopic and macroscopic objects. They are big enough that we can speak of their surfaces and of their surface forces; they are small enough that the population of distinct functioning states depends on the kick of thermal energy. Recognizing this dual nature allows us to bring ideas of colloid and surface science to a class of materials far different from those on which this science is usually practiced.

This duality will be illustrated by several examples. In particular, proteins with large aqueous cavities will be shown to collapse from the pressure of excluded polymers much as colloids in suspension are driven together by the depletion pressures of excluded polymers. The collapsed and open states last for long enough times that the protein is able to take a thermodynamic average over the influence of the bathing medium. The free energies of the distinct states are thermodynamic quantities much as those of macroscopic colloids or surfaces. The hybrid big/small character creates unexpected mechanisms to control biological function. It creates new research opportunities for colloid science.

### **IV. THE STRUCTURE OF AMPHIPHILE MONOLAYERS AT AIR/WATER AND AT OIL/WATER INTERFACES**

**H. Möhwald**

*Max-Planck-Institute of Colloids and Interfaces, Rudower Chaussee 5, D-12489 Berlin, Germany*

Many assemblies in colloid and interfacial sciences are stable or metastable due to the fact that a surfactant monolayer reduces the interfacial energy, and there is much effort to improve the functions of these surfactants. On the other hand there has been a lack of understanding this interfacial layer, predominantly due to a lack of techniques to resolve the structure at the molecular level. The situation has been considerably improved in the last decade, and as most suitable models insoluble amphiphiles at the air/interface were studied.

In the first part of the review it will be shown that amphiphile monolayers possess a rich polymorphism with features from smectic liquid crystals and from ordered states of n-alkanes. The polymorphism is rather general and is further enriched if aliphatic chains are coupled, e.g. in the case of phospholipids. Since order is to be described by many often coupled parameters it is to be studied by various techniques and on different length scales. Thus principles of modern techniques to investigate fluid interfaces will be presented: Synchrotron X-ray diffraction, X-ray and Neutron reflection, fluorescence-, Brewster angle microscopy and imaging ellipsometry, second harmonic generation, and FTIR spectroscopy. Many of the techniques are applicable on soluble monolayers as well as on the oil-water interface. Hence information obtained on these systems will be also presented and compared with those obtained for the insoluble monolayers at the air/water interface. Phase transitions are encountered in these systems too, and also the peculiar domain shapes and periodic domain super lattices due to long-range electrostatic forces are observed. Finally I will present very recent results obtained on increasing the complexity of the system:

- Coupling of polyelectrolytes with monolayers, increases the intermolecular distances and the tilt angle of the chains while preserving local order.
- Ordered phases can be melt, but also the tilt angle can be decreased through contact with alkanes or organic vapours that may incorporate into the ordered or disordered phases.
- Enzyme action at the interface can be controlled via defined manipulation of the structure.

## V. SURFACTANT LIQUID CRYSTALS: MESOPHASE KINETICS; REORIENTATION UNDER SHEAR

Gordon J. T. Tiddy

*Dept. of Chemical Engineering, University of Manchester Institute of Science and Technology,  
PO Box No 88, Manchester M60 1QD, UK*

The aggregate structure and long-range architecture of most surfactant liquid crystals are now well established (lamellar, hexagonal, cubic, nematic, intermediate and "gel"). Moreover, the link between amphiphile type and mesophase structure can be rationalised by considering the hydrophobic chain length/volume and head-group size, both for single surfactants and mixtures. In practical applications it is the kinetics of surfactant phases that are important rather than the equilibrium properties. Almost all of these involve flow and/or dissolution. The next major goal is to describe these processes in terms of molecular structure. Initially this requires the measurement of how flow/dissolution change the aggregate orientation and structure.

Recent X-ray and neutron scattering results on the reorientation of lamellar and hexagonal phases under shear will be described - some of which show shear-induced orientation with the director normal to the direction expected. Optical microscopy of sheared material clearly shows that the flow of mesophases is usually very non-uniform, with marked differences between lamellar, hexagonal and cubic phases.

Recently, a stopped-flow cell for use on the CLRC Daresbury synchrotron X-ray lines became available. The lab.-built detectors and intense radiation allow time-resolution in the ms region. Recent results on the formation of mesophases by mixing nonionic surfactants and aqueous solutions will be presented.

## VI. SCHELUDKO MEMORIAL LECTURE: THIN LIQUID FILMS BEYOND SCHELUDKO

Dotchi Exerowa<sup>1</sup>, Dimo Platikanov<sup>2</sup>, Boryan Radoev<sup>2</sup>, Borislav Toshev<sup>2</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

<sup>2</sup>*Department of Physical Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

The thin liquid films belong to the class of the small systems. They cannot be regarded as having any phase of matter *in mass*. For this reason the long-range interaction forces of different kind are strongly

manifested and they would be in a competition with the short-range interaction forces. Across and along the film the surface forces reveal in different way. All this is of importance for the stability of such subjects as well as of an ensemble of them. The special behaviour of the thin liquid films determine their role for solving many technological, biological, biomedical, etc. problems. All these circumstances were recognized by Prof. A.D. Scheludko more than 45 years ago.

An attempt is presented here for embracing the new experimental results, their interpretation and importance, new experimental methods and techniques and new development of the theory of the thin films based on some novel physical ideas with using the thermodynamic formalism of the grand canonical potential. Examples for applications to some technological and medical problems are considered in brief.

Unique experimental methods are developed for the investigation of the thinnest (black) films: direct measurement of interaction forces; X-ray determination of their thickness and structure; forced rupture by  $\alpha$ - particles; permeability; metastable states in transition; formation of foam films at introducing a surfactant from gas phase. It is paid a special attention to the techniques for direct measurement of interaction forces in microscopic foam films from surfactants, phospholipids and amphiphile polymers as well as the transition from long- to short-range molecular interactions (and the reversal transitions). This allows a more critical testing of the theories of molecular interactions as well as simultaneous identification of the forces acting in thin films (electrostatic, steric, etc.) and estimations of their origin. Barrier and barrierless transitions to bilayer (Newton) black films are found. Stepwise isotherms of multilayer foam films are measured directly. A new approach in the study of amphiphile bilayer (foam, emulsion and membranes) based on short-range interaction forces is introduced and a hole-mediated theory considering the stability and permeability of films from a unified point of view is created. Thus, by means of experimentally measured macroscopic parameters (lifetime, probability for formation, etc.) the microscopic molecular characteristics in the bilayer are determined. Phase transitions in foam bilayers are registered and the relationship with the phase transitions in the bulk is found. The foam bilayer is used as a model for investigating short-range forces in biological structures, the interaction between membranes and cell-fusion. It is also shown that the foam bilayer is a suitable model for studying the alveolar surface and stability. On that basis a clinical diagnostic method is developed for assessment of the human foetal lung maturity and estimation of the efficiency of therapeutical surfactants.

The experimentally established dependence of the thinning rate of foam and emulsion films on their size is much weaker than that required by the classical Reynolds law and many other formulae known from the literature. A theoretical model based on the quasistatic asymmetrically distributed thickness irregularities observed in the films was employed to derive a new equation of thinning. It is in quantitative agreement with the experiment.

The permeation of gas through the black foam films is mainly connected with the surfactant adsorption at the film surfaces: the more ordered monolayers, the less permeable films. The bilayer NBF are about three times less permeable than the thicker threelayer CBF. Data about the structure of the black films have been obtained by X-ray reflectivity measurements. The film tension of the black films has been studied in dynamic and static conditions.

## Abstracts of Papers

### 1.A1 THE RHEOLOGICAL PROPERTIES OF A DENSE SUSPENSION UNDER EXTENSIONAL LOADING

A.Alexandrou<sup>1</sup>, A.Bazilevsky<sup>2</sup>, V.Entov<sup>2</sup>, A.Rozhkov<sup>2</sup> and A.Sharaf<sup>1</sup>

<sup>1</sup>Worcester Polytechnic Institute, Worcester, USA

<sup>2</sup>The Institute for Problems in Mechanics, Russian Academy of Sciences, Russia

The rheological behaviour of dilute suspensions is usually studied in shear; the extensional rheology seems to be never studied experimentally. In the present study suspensions of solid particles were investigated experimentally, both under shear and extension. The method used for elongational investigations is based on the ability of suspensions to form stable thinning filaments (liquid bridges) when they are stretched between two discs. The microrheometer device being utilised was developed in the Institute for Problems in Mechanics. In the device, a fluid sample (approx. 0.1 cu.cm) is placed between two discs. The discs are rapidly moved apart, thus forming a filament. The process of subsequent filament thinning and its collapse was monitored, and the fluid rheological characteristics were computed. A computer analysis of the relevant data was provided using special software. The suspensions under investigation represent the mixtures of sand particles of about 1.5  $\mu\text{m}$  and 15  $\mu\text{m}$  size with glycerine. The volume concentration of the particles ranged from 0 to 0.5. From the result of the work, the following main conclusions are reached: 1. The measured shear flow curves show the Bingham rheological behaviour of the liquids in 0.5-150  $\text{s}^{-1}$  shear rate range (shear stress range 0-500  $\text{Pa}$ ). The shear viscosity and the yield stress increase with growth of the solid volume fraction. 2. The elongational flow curves in the range of stress of 100-1000  $\text{Pa}$  were obtained. It was found that the filament diameter varied linearly with time. This corresponds to the Newtonian rheological behaviour of the suspensions under stretching in the stress range investigated. In this case, the value of the apparent elongational viscosity correlates linearly with the shear viscosity. 3. The dependencies of the apparent elongational viscosity as a function of the solid volume fraction were obtained. These experimental data were fitted by using Krieger-Daugherty equation, which is usually used for shear viscosity data. The results of the fitting are in agreement with the available literature data for shear behaviour of suspensions. 4. Sharp acceleration with a certain filament diameter was discovered. The dependencies of the corresponding critical tensile stresses and the strain rates versus the particle concentration were obtained. These data show the decrease of the critical values with the growth of solid volume fraction, with a significant difference between the cases of suspensions of small and large particles. Attention is drawn to the fact that the suspensions can withstand shear stresses far greater than the tensile critical stresses. 5. Video processing of the filament thinning process has shown that, instead of being uniform along the filament length, decreasing of the filament diameter forms a local neck, and the filament thins faster at the neck region. This phenomenon is more pronounced in the large particle suspensions. The process of the break up of the suspension filament under extension closely resembles that of plastic solids. 6. The results of the work confirm the possibility of using the developed microrheometer device for further investigations of suspension rheology.



### 3.A1 MATHEMATICAL SIMULATION OF SUSPENSION FLOCCULATION BY POLYELECTROLYTES

Ad.A. Berlin<sup>1</sup>, V.N. Kislenko<sup>1</sup>, I.M. Solomentseva<sup>2</sup>

<sup>1</sup>Lviv Polytechnic State University, Lviv, Ukraine

<sup>2</sup>Institute of Colloid and Water Chemistry of NAS, Kiev, Ukraine

A mathematical model of suspension flocculation by polyelectrolytes has been elaborated. It takes account of bridging and non-bridging aggregation of suspension particles, as well as floc break-up under the hydrodynamic action. Non-bridging aggregation occurs due to the simple neutralizing mechanism. Features of bridging and non-bridging aggregation of particles in a suspension has been analyzed with the help of computer simulation. Using experimental data on AgJ sol and poly (methyl vinyl pyridine), we show a good agreement between the mathematical model and the experimental results. It has been determined the rate constants of bridging and nonbridging aggregation, also of floc break-up. It has been established the contribution of each of these both mechanisms into suspension flocculation by polyelectrolyte. The role of the neutralizing mechanism diminishes when molecular mass of polyelectrolyte increases from  $1.4 \times 10^5$  to  $9.3 \times 10^5$ .

### 4.A1 LIGHT-INDUCED PHASE TRANSITIONS IN COLLOID MIXTURES

N.F. Bunkin, A.V. Lobeyev

*Department of Wave Phenomena, Institute of General Physics, Russian Academy of Sciences,  
38 Vavilova street, 11 7942, Moscow, Russia*

The action of short laser pulses on a colloid system, consisting of conjugate phase droplets suspended in a basic phase of stratifying liquid mixture, can be used for quantitative determination of the limits of stability of the mixture with respect to stratification. An important light-induced local phase-separation mechanism, which is realized close to the binodal, includes the processes of the absorption of light, light-induced heating of the mixture, its thermal expansion accompanied by a local increase in the pressure, and finally barodiffusion. In our knowledge, it is the first experimental observation of the light-induced barodiffusion in liquids. Note that the light-induced heating doesn't play a key role for quenching the mixture to the metastable area; in our case the heating is required to induce barodiffusion. In order to determine the spinodal location in the phase diagram, we should stimulate a regime of optical cavitation in liquid due to which an intense intermixing occurs in a dispersed medium. The intermixing provides the uniformity in the concentration distribution within the region of intermixing, and the resultant concentration belongs (at a given temperature) to the labile area.

### 5.A1 QUASIOSCILLATIONS IN THE STRUCTURE OF COLLOID MIXTURE UNDER SPINODAL DECOMPOSITION

N.F. Bunkin, A.V. Lobeyev

*Department of Wave Phenomena, Institute of General Physics, Russian Academy of Sciences,  
38 Vavilova street, 11 7942, Moscow, Russia*

Using a very thin cuvette with a colloid liquid mixture, consisting of conjugate phase droplets suspended in a basic phase of stratifying solution, we observed a quasiperiodic in time transformation of the liquid structure occurring at spinodal decomposition. In our opinion, the observed effect is caused by an interplay between spinodal decomposition and wetting phenomena on the interface liquid-quartz under a deep quench to the labile area. A theoretical model explains the observed dynamics in the framework of analysis of nonlinear diffusion equation, the parameters of which are dependent on the quench depth and the concentration of mixture. An intermediate asymptotic in relation to the initial conditions was found which is an important characteristics of nonlinear dynamic system we studied.

## 6.A1 STABILITY OF WATER DISPERSIONS OF NANODISPERSED ALUMINA AND SILICON NITRIDE IN PRESENCE OF ELECTROLYTES AND POLYMERS

Ermenko B.V., Malysheva M.L., Savitskaya A.N., Bezuglaya T.N.  
*Taras Shevchenko University, Vladimirskaya str. 64, 252017 Kiev, Ukraine*

The new class of materials-ultradispersed powders, obtained by the method of plasm-chemical synthesis (PCS), are widely used in the real technological processes in ceramics formation. One of the main stages of these processes is the preparation of water stable suspensions. Extremely high chemical activity of PCS powders allows to expect some features in these colloid-chemical behavior.

The electrosurface properties and stability of aqueous suspensions of ultradispersed PCS powders  $\text{Al}_2\text{O}_3$  and  $\text{Si}_3\text{N}_4$  ( $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $a = 39$  nm;  $\alpha$ - $\beta$ -, and amorphous  $\text{Si}_3\text{N}_4$ ,  $a = 0.6$   $\mu\text{m}$ ) have been investigated. The surface charge density and electrokinetic potential of samples in aqueous solutions are determined via pH values. The position of IEP and PZC are at  $\text{pH} = 7.5-8.5$  ( $\text{Al}_2\text{O}_3$ ) and  $\text{pH} = 3.5$  ( $\text{Si}_3\text{N}_4$ ). For  $\text{Al}_2\text{O}_3$  the largest value of  $\zeta$ -potential is observed at  $\text{pH} = 3$  (+90 mV) and maximal value of negative  $\zeta$ -potential is at  $\text{pH} = 11$  (-80 mV); for  $\text{Si}_3\text{N}_4$  - at  $\text{pH} = 8$  (-70 mV).

Stability of suspensions was characterized by the critical concentration value of electrolytes which causes coagulation (CCC). CCC of different electrolytes [ $\text{NaNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Na}_2\text{SO}_4$ ] were determined at a wide pH range. The dependencies of CCC on pH are similar to the dependencies of  $\zeta$ -potential on pH. The addition of acid and alkali which leads to the increase of surface charge density and  $|\zeta|$ -potential, leads to the increase in stability. The common character of CCC (pH) dependencies for all used indifferent electrolytes shows that stability of suspensions may be determined by the electrostatic repulsion forces.

CCC values of electrolyte with double charged coagulating counterion are much smaller (~1000 times) than CCC values of electrolytes with single-charged ion. At the same time abnormally high values of CCC for electrolytes with single-charged coagulating ion (300-1800 mmol/l for  $\text{Al}_2\text{O}_3$  and 500-800 mmol/l for  $\text{Si}_3\text{N}_4$ ) allows to confirm that electrostatic repulsion is not the only factor, which determine stability.

To elucidate the mechanism of stability, the potential energy curves of interaction (Van-der-Waals attraction and electrostatic repulsion) of particles were calculated. Calculation shows that potential barrier disappears at a much low concentration of electrolyte (for example, 70-75 mmol/l  $\text{NaNO}_3$  for  $\text{Al}_2\text{O}_3$  at neutral pH and for  $\text{Si}_3\text{N}_4$  in alkali media) than experimental CCC values (300 and 700 mmol/l, correspondingly). Besides this the stability of  $\text{Al}_2\text{O}_3$  suspensions increases with increasing of content of HCl, up to pH 0.6, and it is no opportunity to explain this fact in classic DLVO theory. That is, in our opinion, the evidence of the existence of structural repulsion forces, caused by the "secondary" hydration. Such type of hydration is connected with the hydro-hydroxy polycomplexes of aluminum which existence is connected with the limited dissolution of alumina in water media. These complexes are stabilized by  $\text{NO}_3^-$  and  $\text{Cl}^-$  ions and are disrupted by  $\text{SO}_4^{2-}$ .

The high coagulation ability of 2-1 electrolytes is connected with the specific adsorption of double-charged counterions in DEL.

The abnormally high values of CCC for  $\text{Si}_3\text{N}_4$  suspensions at  $\text{pH} > 8$  is connected, in our opinion, with existence of gel-layers on particle surface, which consist from polysilicic acids, the same ones exist on silica surface (Vigil G., Xu Z., Steinberg S., Israelashvili J. J. Colloid Interface Sci. 1994, V165, N2 p367-385). Such gel-layers provide stability of  $\text{Si}_3\text{N}_4$  suspensions owing to sterical component of disjoining pressure.

## 7.A1 THE INFLUENCE OF SURFACE CHEMISTRY ON THE INTERACTION BETWEEN METAL SULFIDE PARTICLES

Daniel Fornasiero, Stephen Grano, Robert Hayes, Clive Prestidge, Roger St.C. Smart, John Ralston  
*Ian Wark Research Institute, University of South Australia, THE LEVELS SA 5095*

Compared with the relative inertness of metal oxides, the surfaces of metal sulfides are quite reactive. In contact with aqueous solutions, the surfaces of lead sulfide and zinc sulfide undergo spontaneous oxidation, a process which we have studied using a combination of in-situ scanning probe

microscopy and electrical double layer measurements coupled with ex situ surface spectroscopic investigations. The nature of these oxidation products and the extent of oxidation strongly influences the surface hydrophobicity of the metal sulfides. This is reflected in the presence of a hydrophobic force between, say, lightly oxidized zinc sulfide particles. The presence of this hydrophobic force, the first detected between inorganic surfaces, is caused by subtle changes in the zinc to sulfur ratio in the metal sulfide surface layers, and has been directly determined by "colloid probe" atomic force microscopy. Rheological measurements performed on concentrated metal sulfide dispersions also reflect this interaction. Ramifications exist for the electronics and minerals industries.

## 8.A1 SIMULATION OF BREAKUP OF LARGE FLOCS IN FLOWS BY MODIFIED DISCRETE ELEMENT METHOD

**Ko Higashitani and Kenji Iimura**

*Kyoto University, Chemical Engineering Department, Yoshida, Sakyo-ku, Kyoto 606-01, Japan*

It is very important to disperse coagulated particles (flocs) fully in many processes of particle technology. However the details of the breakup mechanism of coagulated particles, especially large flocs, are not known, mainly because there are many ways for a floc to disperse and the data are usually treated statistically. In such a case the simulation becomes a powerful tool to understand the details of the motion of individual particles in a floc.

Here we developed a modified discrete element method (M-DEM) to express the motion of particles in a floc which are in contact with the flow directly and the motion of particles within the floc which are not in contact with the flow. This method was applied to the breakup of a floc composed of a large number of spherical particles in shear and elongation flow fields, and the followings are found.

(1) The dispersion process of coagulated particles are well simulated by the present method; flocs are elongated and then dispersed into several smaller flocs, which looks very similar with the observation reported elsewhere. It is also simulated that the dispersion behavior depends on the size and fractal dimension of flocs.

(2) The dependence of the average size of broken flocs on the strength of the shear field agreed well with the experimental data reported elsewhere. This agreement confirms that the simulation method developed is adequate.

(3) It is predicted that flocs are more easily broken in the elongational flow rather than in the shear flow.

The adequacy of this simulation method indicates that the method will be applicable to estimate the various behavior of coagulated and concentrated flocs.

## 9.A1 KINETICS OF MAGNETIC COLLOID PHASE SEPARATION INDUCED BY AN EXTERNAL MAGNETIC FIELD

**Alexey O. Ivanov and Andrej Yu. Zubarev**

*Urals State University, 620083 Ekaterinburg, Russia*

A kinetic theory of phase separation process in a magnetic colloid made metastable by strengthening of an external magnetic field have been developed. This theory includes the analysis of both the nucleation stage and the intermediate stage of phase transition. In the presence of an external field the elements of a new high concentrated phase are suspended in the low concentrated magnetic colloid in the form of non-spherical drop-like aggregates stretched along the magnetic field direction. The shape of these growing aggregates is convenient to approximate by an ellipsoid of revolution which elongation is dependent on the aggregate volume. In the case of high-elongated ellipsoids the problem of the aggregate growth rate can be solved analytically, under the condition that this growth is limited by a diffusional transport of dispersed ferroparticles to the aggregate surface.

Both the spontaneous origination of initial aggregate nuclei and the probability of their passing over the critical barrier of potential can be treated quite similar to the classical Volmer - Frenkel - Zel'dovich

theory of nucleation. According to this theory the nucleation rate have been obtained as a sharply increasing function of an external field strength. The dependence of the critical aggregate volume on the absolute supersaturation of the parent magnetic colloid and on the interfacial tension have been found.

The further evolution of a system of drop-like aggregates at the intermediate stage of phase transition is investigated under the conditions when both the reduction in metastability and the continuing initiation of new nuclei are taken into account. The aggregates are distributed over volume and the distribution density is governed by the kinetic equation which is complicated by the presence of feed-back between the process of aggregate formation and growth (dependent on a transient degree of metastability) and that of gradual decreasing of metastability by the growing aggregates. The set of basic equations is reduced to the non-linear integral equation for the degree of supersaturation. The approximate solution of this equation is found as function of time. This solution is applicable down to the beginning of Ostwald ripening and defines the diverse characteristics of distribution density which give the total information about the evolution of the aggregate system.

## 10.A1

### DIFFUSION LIMITED GROWTH MODEL OF A SPATIALLY INHOMOGENEOUS COLLOIDAL AGGREGATE

Alexey O. Ivanov

Urals State University, 620083 Ekaterinburg, Russia

Colloidal particles coagulation process leads to the formation and subsequent growth of colloidal aggregates which spatial structure can be considered as inhomogeneous. A mathematical model of single aggregate evolution may be formulated on the basis of intopenetrating media conception. According to this approach the aggregate can be defined with the help of the aggregated particles concentration  $\varphi(t, \mathbf{r})$

coexisting with the non-aggregated particles of concentration  $\rho(t, \mathbf{r})$ .

$$\frac{\partial}{\partial t} \left[ \rho \left( 1 - \frac{\varphi}{\varphi_m} \right) \right] = D \nabla \left[ \left( 1 - \frac{\varphi}{\varphi_m} \right)^\alpha \nabla \rho \right] - \frac{\partial \varphi}{\partial t}, \quad \frac{\partial \varphi}{\partial t} = a \rho \varphi \left( 1 - \frac{\varphi}{\varphi_m} \right) - b \varphi (\varphi_m - \varphi), \quad a, b - \text{const},$$

$$\varphi(t, \Sigma^-) \frac{d\Sigma}{dt} = D \nabla \rho(t, \Sigma^+) - D \left[ 1 - \frac{\varphi(t, \Sigma^-)}{\varphi_m} \right]^\alpha \nabla \rho(t, \Sigma^-)$$

The diffusion motion of "bonded"  $\varphi$ - particles may be neglected in comparison with motion of "free"  $\rho$ - particles. The diffusion flux of the latter is hindered by the presence of  $\varphi$ - media and falls to zero in the regions of closely packed aggregated particles with concentration  $\varphi_m$ . The intertransformation of  $\varphi$  and  $\rho$  intopenetrating media is convenient to consider with the help of non-linear mass exchange terms under the condition when both the processes of particles gaining to the aggregate and loosing from the aggregate are taken into account.

The volume occupied by the aggregate is bounded by a surface  $\Sigma$ , the increasing of this volume (the aggregate growth) is described by the moving boundary condition for the normal surface rate  $d\Sigma/dt$ .

In the case of a slow aggregate growth, the two kinds of decision have been found:

-the first one is characterized by a constancy of the aggregated  $\varphi$ - particles inside an aggregate ( $\varphi \sim \varphi_m$ ) and by a classical diffusion-limited growth rate. Such aggregates arise during a phase separation process in colloidal systems and are similar to liquid drops in a supersaturated gas.

-the second kind of the decision reminds a fractal cluster and contains a central dense "core" and a surrounding zone of decreasing  $\varphi$ - particles concentration, in which the aggregate becomes more and more friable. In this area the concentration of aggregated particles varies similarly to power function  $\varphi(r) \sim r^{-\beta}$ , where the fractal cluster dimension  $\beta$  represents the slow time dependent function.

## 11.A1 ISOPERICHORIC FOCUSING PHENOMENA IN BIDISPERSE NANOSIZE PARTICLE SUSPENSIONS: THEORY, EXPERIMENTAL IMPLEMENTATION, AND APPLICATIONS IN FIELD-FLOW FRACTIONATION

Josef Janca<sup>1</sup> and Milena Spirkova<sup>2</sup>

<sup>1</sup>Université de La Rochelle, Pole Sciences et Technologie, Avenue Marillac,  
17042 La Rochelle Cedex 01, France

<sup>2</sup>Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2,  
16206 Prague 6, Czech Republic

Contrary to an old axiom that a density gradient forming liquid in isopycnic focusing should behave as continuum regarding the discrete focused species, the theory [1] predicts the focusing without imposed sudden difference between the size of the focused and density gradient forming species. This prediction was verified experimentally by the isopycnic focusing of polyaniline (PANI) based component of a bidisperse nanosize particle suspension of PANI and silica [2].

The colored polyaniline-polyvinylpyrrolidone composite (PANI-PVP) nanosize particles were focused in a colorless density gradient formed by colloidal silica-PVP composite particles under conditions of thin-layer isopycnic focusing (TLIF) centrifugation. The particle size distributions of the PANI-PVP and silica-PVP composites were very close and partly supersposed thus forming a bidisperse suspension.

The macrophotograph of the steady-state zone of the PANI-PVP particles focused in bidisperse mixture with silica-PVP is shown in Fig. 1 together with the comparison of the experimental and theoretical concentration distributions of the PANI-PVP within the focused zone.

The model focusing experiment described in this study proved that the isopycnic focusing appears in a suspension mixture of the two different but close sizes colloidal particles and that this phenomenon is correctly described by our theoretical model. These results are of crucial importance for the focusing field-flow fractionation as demonstrated by model separations.

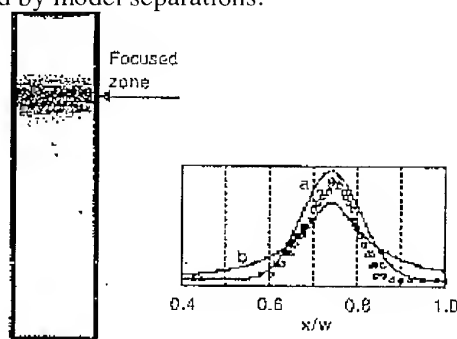


Fig. 1. Scannerized macrophotograph image of the focused zone and the comparison of the theoretical (-) and experimental (o) steady state concentration distributions. Theoretical curve (a) corresponds to a hypothetical monodisperse fraction while the curve (b) corresponds to the real polydisperse fraction.

1. Janca J., Audebert R.: *J. Appl. Polym. Sci., Appl. Polym. Symposia* 52, 63 (1993).

2. Janca J., Spirkova M.: *Collect. Czech. Chem. Commun.* 61, 819 (1996).

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## 12.A1 INTERACTION OF PROTEINS WITH DISPERSED SILICA IN AQUEOUS SUSPENSIONS

O.A. Kazakova, V.M. Gun'ko

*Institute of Surface Chemistry, Kiev, Ukraine*

Quantum-chemical modelling of proteins interaction with dispersed silica in aqueous suspensions provides additional means in the study of these systems. Solvation effects for dipeptides (Lys-Gly, Asp-Gly, Glu-Gly, His-Gly) have been investigated by AM1-SM1 method. Studied dipeptides corresponded to the

fragments of bovine serum albumin, which adsorption on fumed silica in aqueous suspensions was studied. The interaction of peptides in molecular and zwitter-ion shapes with the  $\equiv \text{Si-OH}$  groups on silica surface was examined. It was determined that the adsorption of peptides begins from  $\equiv \text{SiO(H)}\dots\text{HOC(O)R}$ ,  $\equiv \text{SiO(H)}\dots \text{HNR}$ -bonds formation. Zwitter-ion's shape of dipeptides are not stable in the gas phase. However, they become more stable on the surface due to hydrogen bonding with  $\equiv \text{Si-OH}$  surfacial groups. These effects are all the more significant in aqueous suspensions.  $\equiv \text{SiO}^-\dots\text{H}^+\text{NR}$ ,  $\equiv \text{SiO(H)}\dots\text{H}^+\text{NRCOO}^-$ -bonds was found to make a maximum contribution to the stabilization of adsorption complexes of dipeptides on silica. Again,  $\text{H}^+$ -transfer from  $\equiv \text{Si-OH}$  surfacial groups to protein's aminogroup can be efficient in suspensions due to the stabilization of ions. It allows to explain the strong protein adsorption by dispersed silica particles from solution. Results of theoretical simulations and experimental studies are in good agreement.

### 13.A1 INVESTIGATIONS IN THE FIELD OF PROPERTIES AND APPLICATION OF GEL-LIKE INORGANIC SYSTEMS

Kuprienko P.I.

*Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine*

A number of technical tasks to be solved (colloid-chemical materials science, oil extraction, purification of water etc.) the necessity of attaching special structural and mechanical properties to disperse systems emerges. Gel-like additives applied with the aim (PVA, dextrin, soaps, copolymer of styrene with the salts of maleic acid) have not enough structurizing ability and protective ability to admixtures of coagulators. Therefore, to extent the assortment of the substances, to search advanced stabilizers, plasticizers, filmforming and adhesive agents for their utilization as ingredients of technical suspensions is of great importance. Herein, the main interest is to inorganic gel-like systems.

Inorganic gel-like systems are produced by surface modification of natural and synthetic silicates as well as disperse systems based on them. It was shown by methods of rotational viscosimetry and potentiometric titration that rheological parameters of initial aqueous dispersions were changed sharply when modifying agents were added. Enhancement of structure formation (gelling) inside a system is caused by ionic modification of interface, complex compounds and colloidal disperse phase formation.

It is worth to note that each individual mechanism of gelling has its own peculiarities. Abnormal dependences of shear stress on rate of deformation and elective viscosity- on shear stress can be explained by fractional structure of the gels. In the majority of cases when gel-like systems are synthesized the interaction between disperse phase and modifier takes place accompanied by surface compounds formation.

Developed by author gel-like systems and ways of modification were tested in technology of oxide ceramics production, soldering pastes manufacture and are now applied in technology of unbaked luminescent coatings formation for gas-discharge lamps.

Application of the gel-like inorganic systems extends the opportunity of ecologically safety engineering creation.

### 14.A1 EFFECTS OF PARTICLE INTERACTIONS ON SIZE MEASUREMENT BY SEDIMENTATION FIELD FLOW FRACTIONATION WITH PROGRAMMING FIELD

Yasushige Mori and Masahiro Harada

*Dept. of Chem. Eng. & Mater. Sci., Doshisha University, Kyotanabe, Japan*

Sedimentation field-flow fractionation (SdFFF) has a high resolution over a wide range of particle size compared with other methods of size determination of colloidal dispersions. However the particle sizes calculated by the theory of Giddings from the experimental results of SdFFF are underestimated, comparing with those determined by other techniques, if the carrier solution with low ionic strength was used. To explain this phenomenon, this study discussed the perturbation behavior of the retention time by the particle-wall and particle-particle interactions due to the electrostatic repulsive and van der Waals attractive forces using DLVO theory, and by the contribution of the retardation of particle motion in the shear flow.

When SdFFF was operated at a constant field strength during the measurement (CF-SdFFF), the theory of Giddings could be only applied to estimate particle size at the experimental conditions of the smaller particles than 600 nm diameter and the aqueous solution with higher ionic strength than 1 mM. The interactions mentioned above should be considered at the other conditions of CF-SdFFF.

When the field strength was decreased exponentially in the course of the experimental period, that is programming field mode (PF-SdFFF), the analytical time for particles with a wide range of sizes could be decreased without the decrease of the size resolution. The particle size could be predicted by the theory of Giddings, if using the carrier solution with 2.25 mM ionic strength. However, under a low ionic strength condition of a carrier solution, the calculation to particle sizes from the observed retention times needed the retention theory considering the interactions mentioned above.

## 15.A1 SURFACE CHEMISTRY AND RHEOLOGICAL BEHAVIOUR OF TITANIA PIGMENTS

Gayle E. Morris, William M. Skinner, Roger St. C. Smart

*Ian Wark Research Institute, University of South Australia, The Levels, S. A., 5095, Australia*

Titania pigments are widely used in the paint, plastics, paper and pharmaceutical industries. The pigments typically consists of a polycrystalline titania core particle of  $\sim 0.3 \mu\text{m}$  coated with thin inorganic or organic layers. The inorganic or organic surface layers enhance both durability of titania against UV radiation and pigment dispersability. The synthetic titania (rutile) core, which is aluminium doped, provides a high refractive index substrate that is ideal for absorption or reflection. Doping of titania with aluminium is carried out in order to circumvent the UV induced photoreduction of  $\text{Ti}^{4+}$  which degrades pigment optical properties such as brightness and opacity. Characterisation of the titania substrate is of importance for the subsequent application of the coating layers. Investigation of the surface properties and rheological behaviour of titania pigment dispersions of varied aluminium concentrations were undertaken; the influence of pH, electrolyte concentration and cationic species on the level of dispersion, as defined by yield values and viscosities, are reported.

The variation in rheological properties with pH and cationic species correlated well with the change in the titania surface properties, determined from microelectrophoresis, dissolution studies and X-ray photoelectron spectroscopy (XPS) surface chemical analysis. Titania suspensions with maximum yield stress and viscosity occurred at and near the isoelectric point (iep). At a pH where the magnitude of the electrophoretic mobility of the titania is high, a low viscosity dispersed suspension was obtained. Aluminium doping shifted the pH of maximum yield stress of titania to a higher pH; an effect attributed to the presence of an alumina surface layer.

## 16.A1 EFFECT OF METHANOL ON STABILITY OF AgI HYDROSOL PROTECTED BY POLYACRYLAMIDE

Waldemar Nowicki and Grazyna Nowicka

*A. Mickiewicz University, Faculty of Chemistry, Poznan, Poland*

Stability of colloidal suspension protected by polymer can be modified by changing the solvency of the stabilizing polymer in the dispersion medium. With deteriorating solvent quality, the attractive forces between adsorbed polymer chains and the London- van der Waals forces acting between the particle cores lead to flocculation of the suspension.

The paper reports results of study on the effect of addition of a non-solvent on colloidal stability of silver iodide hydrosol protected by polyacrylamide (PAAm) which is one of the most important water-soluble polymers from the point of view of technological applications, and has been widely used in processes of stabilization and destabilization of suspensions. PAAm can be precipitated from aqueous solutions by addition of methanol. The effect of methanol addition on stability of the system was characterized by measurements of the stability coefficient (defined as the ratio between the turbidities of samples with and without alcohol) performed in a wide range of methanol volume fraction  $x_{\text{MeOH}}$  in the

dispersion medium. Measurements were performed at various concentration of an indifferent electrolyte in the system since in polar media, in addition to steric effects, electrostatic interactions also affect the suspension stability. The properties of PAAm in water-methanol-electrolyte mixtures were also examined.

The results indicated that in the absence of electrolyte, the non-solvent induced flocculation of AgI sol, protected by PAAm, began to take place at  $x_{\text{MeOH}}$  much higher than it would result from the  $\Theta$ -solvent composition. On the other hand, in the presence of electrolyte, the lowest  $x_{\text{MeOH}}$  needed to induce flocculation corresponded roughly to the value following from the  $\Theta$ -solvent composition. However, in the presence of electrolyte a maximum was observed in the dependencies of the stability coefficient on  $x_{\text{MeOH}}$ , in the range of methanol concentration higher than that following from the  $\Theta$ -solvent composition. The height of the maximum increased with the rise in the polymer to particle concentration ratio and decreased when the particle size and ionic strength of the medium increased. The appearance of the maximum has been proved to be related to the microphase separation of the non-adsorbed polymer.

## 17.A1 ROLE OF CONFORMATION AND ORIENTATION OF SURFACTANTS AND POLYMERS IN CONTROLLING DISPERSION/FLOCCULATION AND DEPOSITION IN AQUEOUS AND NON-AQUEOUS SUSPENSIONS

P. Somasundaran

*Langmuir Center for Colloids & Interfaces, Columbia University, New York, NY 10027*

Surfactants, polymers and their mixtures are widely used in important industrial processes for dispersion/flocculation, deposition, flotation, dewatering, paints and oil recovery. In this work, the role of adsorbed layer microstructural properties, namely their conformation and orientation at solid-liquid interface, in controlling dispersion properties is examined. A multi-pronged approach involving the use of fluorescence, ESR, Raman and NMR spectroscopic techniques along with measurements of surface charge and hydrophobicity was used to explore the structure of adsorbed layer

The adsorption isotherm of sodium dodecyl sulfate on alumina in aqueous solution interface shows different regions corresponding to different adsorption mechanisms. The suspension stability also displayed significant changes concomitant with changes in the structure of the adsorbed layer. Fluorescence spectroscopy coupled with hydrophobicity and zeta potential measurements has enabled us to elucidate the evolution of the adsorbed layer and formation of colloid surface layers. When polymers are used their conformation can be manipulated by changing solution conditions such as pH and/or by the addition of a secondary polymer or surfactant. Such manipulation can be used to obtain desired levels of flocculation, stabilization, deposition or wettability.

In nonaqueous media, adsorption was found to depend on the solid-solvent-solute interactions as expressed by an effective interaction parameter  $\delta_{\text{eff}}$ . The suspension stability was dependent on the amount adsorbed and the packing of molecules in the adsorbed layer. Presence of even trace polar impurities was found to have a critical effect on the suspension stability. For example, trace amounts of water were found to cause a significant enhancement of stabilization of alumina-cyclohexane suspension in the presence of adsorbed surfactant layers. However, at higher concentrations water induced rapid flocculation in these systems. Hydrophobic polymers were found to be effective stabilizers for alumina in both aqueous and nonaqueous media. In this case the polymer adsorbed at the interface in different orientations with the lyophilic side chains dangling into the solution to provide steric repulsion and thus stabilization.

## 18.A1 PROTEIN INTERACTIONS IN SOLUTION INVESTIGATED BY LIGHT AND NEUTRON SCATTERING

O.D.Velev, E.W.Kaler and A.M.Lenhoff

*Department of Chemical Engineering, University of Delaware, Newark, DE 19716, USA*

The effect of pH and electrolyte concentration on the protein-protein interactions in solution was investigated with the use of static light scattering (SLS) and small angle neutron scattering (SANS). The



experiments were carried out with lysozyme and chymotrypsinogen. Very good agreement between the values of the virial coefficients by SLS and SANS was obtained without any adjustable parameters.

The virial coefficients are positive at low electrolyte concentration and pH. They decrease and become negative when the pH is increased. At high salt concentration, the coefficients become slightly negative and depend weakly on the pH. The virial coefficients for lysozyme always decrease with increasing electrolyte concentration. Alternatively, with chymotrypsinogen there is a crossover point (at pH=5.2) above which the virial coefficients decrease with increasing of the ionic strength. The data are interpreted in terms of the effect of pH on the protein charge and dipole moment and their impact on the repulsive and attractive electrostatic interactions. Simple experimental tests with lysozyme show that the values of the virial coefficients can be qualitatively correlated with protein precipitation and crystallization behaviour.

## 19.A2 THE OSMOTIC PRESSURE OF ELECTROSTATICALLY STABILIZED COLLOIDAL DISPERSIONS - A WIGNER-SEITZ CELL APPROACH

W. Richard Bowen and Paul M. Williams

*Biochemical Engineering Group, Department of Chemical Engineering, University of Wales Swansea, Singleton Park, Swansea, SA2 8PP, UK*

A mathematical model for predicting the osmotic pressure of electrostatically stabilized colloids has been developed. The model is based on detailed descriptions of the colloidal interactions within an electrostatically stabilized dispersion. Electrostatic interactions are accounted for by a Wigner-Seitz cell approach including a numerical solution of the non-linear Poisson-Boltzmann equation. London-van der Waals forces are calculated using a computationally efficient means of approximating screened, retarded Lifshitz-Hamaker constants. Configurational entropy effects are calculated using an equation of state giving excellent agreement with molecular dynamic data.

These descriptions of colloidal interactions are used to develop an *a priori* model, with no adjustable parameters, that allows quantitative prediction of the osmotic pressure of colloidal dispersions as a function of zeta potential (and hence pH), colloid size, ionic strength and colloid concentration. The model shows good agreement with literature experimental data for the osmotic pressure of the protein bovine serum albumin (BSA).

A charge regulation model for the BSA surface has also been developed from knowledge of the amino acid groups giving rise to the protein charge. A comparison of zeta potentials calculated from this model with experimentally determined values for dilute BSA dispersions shows good agreement for a wide range of conditions. The charge regulation model has also been incorporated into the osmotic pressure prediction, resulting in excellent agreement between theory and experiment.

## 20.A2 FILM FORMATION OF LATEX DISPERSIONS - AN INVESTIGATION BY OPTICAL METHODS

Alexander Du Chesne<sup>1</sup> and Carsten Heldmann<sup>2</sup>

<sup>1</sup>*Max-Planck-Institut für Polymerforschung, PF 3148, 55021 Mainz, Germany*

<sup>2</sup>*Hoechst-AG, 65926 Frankfurt am Main, Germany*

Concern for the environment dictates to decrease the emission of organic solvents into the atmosphere. Hence, the research on aqueous dispersions of latex for water borne coatings (latex films) gained actuality during the last years. In order to replace solution cast films in remaining fields of their application, the performance of latex films has to be improved. This requires a better understanding of the process of film formation from latex dispersions.

Latex particles of narrow size distribution tend to crystallise upon drying. Their packing behaviour, particle deformation and coalescence (film formation) can be studied by optical methods, if the size of the particles is of the same order of magnitude as the wavelength of the light used for detection.

We synthesized dispersions of polyvinylacetate and of polyacrylate latices which meet these requirements. Under distinct drying conditions it is possible to slowdown the processes of packing and film

formation. Furthermore, the different stages of film formation appear locally separated in phases which can be visualized in an optical microscope and which are large enough to detect packing parameters by using a focused laser beam.

The processes of latex particle packing, deformation and coalescence are studied in time as a function of temperature, latex composition and size.

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## **21.A2            ACOUSTIC AND ELECTROACOUSTIC SPECTROSCOPY OF CONCENTRATED DISPERSIONS**

**A.S. Dukhin and P.J. Goetz**

*PenKem Inc., 341 Adams St., Bedford Hills, NY, USA*

Both acoustic and electroacoustic spectroscopy are related to a sound propagation through a concentrated dispersed system. An acoustic spectrometer measures only the changes in the properties of the sound wave, whereas an electroacoustics spectrometer deals with coupling between electrodynamic phenomena and the sound wave pressure field. Acoustic and electroacoustics spectroscopy are independent methods. As one would expect, each technique has advantages and disadvantages. Acoustic spectroscopy cannot give a complete characterization of the disperse system because it is able to characterize only the particle size distribution. Electroacoustics spectroscopy, in certain cases, can provide a more complete characterization, but requires assumptions about the sample which may not be valid, particularly in concentrated systems. A new approach is suggested and accomplished here which combines acoustic and electroacoustic spectroscopy and eliminates the disadvantages of both.

## **22.A2            ELECTROACOUSTICS - PRESENT ACHIEVEMENTS AND FUTURE TRENDS**

**Robert J. Hunter**

*School of Chemistry, University of Sydney and Colloidal Dynamics Pty Ltd, Australian Technology Park,  
Sydney, Australia*

Electroacoustics refers to those processes, applied to colloidal or electrolyte systems, in which an applied electric field induces a resulting sound wave response (the ESA effect), or a sound wave induces a macroscopic potential difference in a suspension (the CVP effect). It is now well established that by making measurements at a number of frequencies, and taking advantage of the complex nature of the signals involved, one can simultaneously measure both the size of the colloidal particles and the effective (electrokinetic) charge on the particle surface. The technique has been applied to a variety of solid suspensions such as the metal oxides, the clay minerals and other insoluble silicates, metal sulfides, calcium carbonate, silicon nitride, and other important industrial colloids. The method is also ideal for the study of emulsion systems, chiefly because it can be applied to systems of essentially any particle concentration. The ability to make measurements without dilution is especially important in emulsion systems because dilution almost invariably alters the adsorption equilibrium between surface and bulk.

Very high zeta potential systems, which cannot be measured properly by d.c. techniques are more readily handled by these high frequency techniques and even semiconductor materials can be handled effectively. There are some systems for which the simple double layer model is inappropriate and electroacoustics, used in conjunction with dielectric relaxation, is able to provide useful information, not only on the particle size and charge but also on particle shape.

The ability of these methods to provide real time information in concentrated colloidal and emulsion systems makes them ideal for the development of on-line process monitoring and control devices and this is undoubtedly the way of the future.

## 23.A2

## HOW HOMOGENEOUS ARE "HOMOGENEOUS DISPERSIONS" ?

Norio Ise

*Central Laboratory, Rengo Co., Ltd., Ohihiraki, Fukushima, Osaka 553, Japan*

The photographic records by the Lang method in X-ray topography of the global internal structure of dilute polymer latex dispersions showed the coexistence of ordered domains and disordered regions of particles [1]. The video imagery study revealed trajectories of disordered particles quite different from those of ordered particles, suggesting at least two diffusion modes from homogeneous dispersions [2]. By using confocal laser scanning microscope (CLSM) the concentration of ionic latex particles was found to be higher in the distance range between 5 and 50  $\mu\text{m}$  from the like-charged interface than in the bulk [3]. The positive adsorption was enhanced when the interface charges were increased [4]. The CLSM observation revealed the presence of large and stable voids in apparently homogeneous dispersions [5]. The one-dimensional ultra-small-angle X-ray scattering (USAXS) study showed five orders of Bragg diffraction, suggesting the formation of a single crystal (bcc) of colloidal silica particles at 3.76 vol % in water [6]. The four- and six-fold symmetries were found [7]. This indicates that the (110) planes, most densely packed ones for bcc, were always parallel to the container glass wall, in conformity with the positive adsorption. The closest interparticle Bragg distance was definitely shorter than the average spacing, suggesting contraction during crystallization and hence particle-particle attraction. The two-dimensional USAXS study of the silica dispersions displayed 22 sharp peaks below  $203^\circ$  (diffraction angle) [8], confirming the results from the 1-D USAXS. The USAXS study of poly(chlorostyrene styrenesulfonate) [PCSS] particle dispersions again showed the closest interparticle spacing being smaller than the average spacing, indicating non-space-filling nature of the structure and hence the coexistence of two regions of high and low particle densities [9]. In conformity with this result, void structures were confirmed by CLSM investigation for the PCSS dispersions. Monte-Carlo simulation was carried out using the purely repulsive DLVO potential and the Sogami potential containing a short-range repulsion and long-range attraction. The void structures could be reproduced by the Sogami potential but not by the DLVO theory [9]. These studies suggest positively that there exists attraction between like-charged particles and between like-charged interface and particles, causing structural inhomogeneity in colloidal dispersions.

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## 24.A2

## RECONDENSATION MODEL FOR DISPERSIONS IN ONE DIMENSION

N.I. Lebovka<sup>1,2</sup>, V.V. Mank<sup>2</sup>, V.P. Makovetsky<sup>3</sup>, N.S. Pivovarova<sup>3</sup><sup>1</sup>*Inst. Biocolloidal Chem., NAS of Ukraine, 42 blvr. Vernadskogo, Kyiv, 252142, Ukraine*<sup>2</sup>*Kyiv Mogyla Academy University, 2 vul. Scovorody, Kyiv, 252145, Ukraine*<sup>3</sup>*Sonar, Kyiv, 252145, Ukraine*

The coarsening processes (or Ostwald ripening, 1908) play an important role in establishment of dynamics of the droplet size distribution function in concentrated dispersions. This phenomenon, including the substance transfer from small to large droplets, was experimentally observed in various systems, for example, in crystal dispersions, emulsions, aerosols, etc. The theoretical description of this phenomenon is somewhat complicated by difficulties connected with adequate simulation many-body interactions and computations of the mutual influence of the diffusion fields around the droplets, so at present it is available only for the case of diluted dispersion under the isothermal conditions (Lifshitz-Slyozov theory, 1961).

In this work we have studied the one-dimensional recondensation model in concentrated dispersions under the condition of periodical changes of temperature. At initial moment each lattice cell was occupied with one droplet. The initial distribution function of droplet masses  $f(m)$  had a stepwise form with the step width  $\Delta m$ . The periodical boundary conditions were applied to lattices with the total length of up to  $10^4$ . The

temperature varied with time in a sinusoidal (with  $dT$  amplitude and  $t_p$  period) manner. On every elementary time-step the droplet substance redistribution over the cells in accordance with droplet surface areas ( $\sim m^{2/3}$ ) was executed. Here, the possibility of droplet substance reallocations among the  $z$  nearest neighbours was taken into account. The stages of condensation different in the rate of processes occurring at such stages, as well as the chances in average mass of dispersed droplets, their number and profile of  $f(m)$  distribution function versus time dependence were analyzed and shown to depend critically on assumed model of agitation, controlled by the value of  $z$  parameter. The determinative character of influence of the heating-cooling cycles alternation frequency at recondensation processes was demonstrated.

## 25.A2 DYNAMIC MOBILITY OF SPHERICAL COLLOIDAL PARTICLES IN CONCENTRATED SUSPENSIONS

Hiroyuki Ohshima

*Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science,  
Science University of Tokyo, 12 Ichigaya Funagawara-machi, Shinjuku-ku, Tokyo 162, Japan*

The electroacoustic measurement is a new technique for the electrokinetic analysis of colloidal dispersions. O'Brien (*J.Fluid.Mech.* 190, 71 (1988)) demonstrated that the electrokinetic sonic amplitude (ESA) is proportional to the dynamic electrophoretic mobility of colloidal particles in an applied oscillating electric field. Mangelsdorf and White (*J.Chem.Soc.Faraday Trans.* 88, 3567 (1992)) obtained the full electrokinetic equations governing the dynamic electro-phoresis of spherical colloidal particles as well as their numerical computer solutions. Ohshima (*J.Colloid Interface Sci.* 179, 431 (1996)) derived a general dynamic mobility expression from Mangelsdorf and White's electrokinetic equations and obtained accurate simple analytic formulas suitable for numerical calculation for the dynamic electrophoretic mobility and the ratio of dynamic and static mobilities which are applicable for all  $\kappa a$  ( $\kappa$  = Debye-Hückel parameter and  $a$  = particle radius) at zero particle permittivity and low zeta potentials.

In the present paper we consider a more practical electrokinetic problem of dynamic electrophoresis of a swarm of colloidal particles in concentrated suspensions under an applied oscillating electric field and obtain a general expression for the dynamic mobility on the basis of Kuwabara's cell model (*J.Phys. Soc. Japan*; 14, 527 (1959)). The mobility depends on the particle zeta potential  $\zeta$ , the frequency  $\omega$  of the applied oscillating electric field,  $\kappa a$ , and the particle volume fraction  $\phi$  (or the porosity  $\epsilon$ ). In the limit of  $\omega = 0$  (static electrophoresis), the obtained mobility expression tends to a static mobility expression derived by Levine and Neale (*J.Colloid Interface Sci.*, 47, 520 (1974)) for low zeta potentials and to that by Kozak and Davis (*J.Colloid Interface Sci.*, 129, 166 (1989)) for the case of non overlapping double layers. In the limit of the single-particle problem ( $\phi \rightarrow 0$ ), the results reproduce those derived by O'Brien, Mangelsdorf and White, and Ohshima. A simple analytic mobility expression is also derived.

## 26.A2 EFFECT OF THE DOUBLE LAYER IONIC DISTRIBUTION ON THE STRUCTURE AND PHASE DIAGRAM OF CHARGED NANOMETRIC PARTICLES

J. Persello<sup>1</sup>, A. Foissy<sup>1</sup> and B. Cabane<sup>2</sup>

<sup>1</sup>*Laboratoire d'Electrochimie et des Systèmes Microdispersés, 25030 Besançon, France.*

<sup>2</sup>*Equipe mixte CEA-RP, Rhône-Poulenc, 93308 Aubervilliers, France.*

In this work, the relations between surface chemistry and colloidal stability in concentrated dispersions, have been investigated in two particular examples of well characterized charged; nanometric dispersions of titanium dioxide and nanometric dispersions of silica. These dispersions are typical of the problems encountered with concentrated nanometric oxide dispersions: they are stable only in a limited range of pH and display a wide range of structural and rheological behaviour. We present experimental results quantifying the phase diagram and structural transition in the two systems and we examine the role played by the microscopic ionic distribution at the surface in the phase formation.

The distribution and density of surface groups at the surface of the particles were investigated through titration of the surface groups with either base or acid. The data were interpreted according to the "MUSIC" model developed by Van Riemsdijk and co-workers. The results on the  $\text{TiO}_2$  sols indicate that there are different surface states and surface reactions gave different results depending on the range of pH where the titration were performed. In contrast, silica particles are amorphous particles and the ionised sites are homogeneous distributed around the particle over all pH range.

The particle volume fractions,  $\phi$ , of dispersions were adjusted through the osmotic stress technique pioneered by A. Parsegian et al. The particle volume fractions of dispersions equilibrated through this technique could be set between  $\phi = 0.01$  and  $\phi = 0.70$ . For 20 nm particles, the average face to face distance between the particles could be set between 65 nm to near contact (0.3 nm).

Small-angle neutron and X scattering (SANS and SAXS) and light scattering have been used to study the interactions between particles in both silica and titanium oxide sols covering a range of volume fraction from 0.01 to 0.55 and electrolyte concentration from  $10^{-3}$  to 0.1 mole/l. In a typical experimental situation, a osmotic pressure may be applied to the entire dispersion, and the spacing between the particles is monitored with SANS or SAXS.

The central result of our work is the phase diagrams of the two systems. We compare our experimentally determined phase diagrams with recent analytical models. For the silica sols, we find good agreement between our experimental results and the theoretical predictions for the solid-liquid transitions. We may concluded that structure formation was due to Coulombic repulsions.

For the  $\text{TiO}_2$  sols, raising the osmotic pressure beyond the ionic double layer overlap region causes in a first time a first-order phase transition and in the limit of high concentration of particles, causes the irreversible aggregation of the particles. The details of the phase behaviour depend on the ion distribution on the surface and were governed by the short range interactions. We suggest that the structure formation was due to the aggregation of the  $\text{TiO}_2$  particles through non charged crystal faces.

## 27.A2

### ROLE OF INTERPARTICLE FORCES AND SUSPENSION STRUCTURE ON RHEOLOGY

Y. Rabinovich<sup>1</sup>, A. Dogariu<sup>2</sup>, A. Zaman<sup>1</sup>, B. Moudgil<sup>1</sup>, R. Rajagopalan<sup>1</sup>, H. El-Shall<sup>1</sup>

<sup>1</sup>Engineering Research Center for Particulate Science and technology, University of Florida,  
Gainesville, FL, USA

<sup>2</sup>CREOL, University of Central Florida, Orlando, FL, USA

Experimental investigations of the microstructure and interparticle forces in colloidal suspensions are integrated with rheological studies for better understanding. The microstructure of colloidal dispersions is of crucial importance for a large class of industrial applications. In this respect, the light back-scattering techniques are most attractive because of their non-intrusive character. Most of the previous work has been devoted, however, to weakly scattering colloids or to non-aqueous dispersions with strong forward multiple light scattering. We have developed an enhanced back-scattering (EBS) technique to investigate the structure of concentrated optically opaque particles. This technique is attractive since it can be used as a direct probe of microstructure in industrial environment and, further, as an optical complement of other probing techniques such as rheological measurements of structure. EBS uses a back-scattering mode, which requires only one-side open geometry as opposed to classical forward-scattering and transmission techniques. EBS can be used for both liquid-like or solid-like media.

We used the EBS method to investigate the structure of model silica dispersions at various pH and electrolyte concentrations as a function of volume fraction  $\Phi$  of particles. The transport mean free path  $L$  is calculated as a function of  $\Phi$  using experimentally determined angular distribution of intensity. Comparison of this with theoretically calculated  $L$  allowed to evaluate possible pair correlation functions. The dependence of  $L$  on various parameters is explained from the point of view of the interparticle forces. The interparticle forces between a silica sphere and a plate were also measured experimentally using atomic force microscopy. The critical value of pH at which interaction potential barrier disappears is determined. The optical and force measurements are compared with rheological data, and it is shown that the rheological, structural and force characteristics are correlated with each other. The ranges of  $\Phi$  and values of  $\Phi$ , where structural transitions take place, are determined.

## 28.A2

FILM FORMATION STUDIES OF LATEX DISPERSIONS  
BY SOLID STATE NMRJ. Rottstegge<sup>1</sup>, K. Landfester<sup>1</sup>, M. Wilhelm<sup>1</sup>, C. Heldmann<sup>2</sup>, H. W. Spiess<sup>1</sup><sup>1</sup>Max-Planck-Institut für Polymerforschung, P. O. Box 3148, 55021 Mainz, Germany<sup>2</sup>Hoechst AG, Frankfurt, Germany

Latexes consist of polymer particles, stabilized and dispersed as colloids in an aqueous phase using surfactants. Important applications are adhesives, paper coatings and paints. Latex systems based on poly(acrylate) and poly(vinylacetate) containing different emulsifiers and copolymers have been investigated with respect to their film formation behaviour by <sup>1</sup>H-, <sup>2</sup>H-, <sup>13</sup>C- Solid State NMR techniques.

During the drying process in the first stage of the film formation process, the loss of water causes an increase in polymer concentration so that the spherical polymer particles have to pack. The latex particles are deformed to a compact particle array. Final interdiffusion leads to a homogeneous film. For samples with various solid contents we investigated the different stages of film formation process by <sup>1</sup>H-, <sup>2</sup>H-, <sup>13</sup>C- Solid State NMR. We mainly concentrated our investigations on the early stages where the samples still contained water.

Various types of surfactants based on poly(ethylene oxide), sodium sulfonates, ionic and nonionic copolymers have been used to detect characteristic changes in the samples. Different types of mobile water located at ionic and nonionic molecular groups of the surfactants and copolymers have been found at the polymer-water interface. The measurements (<sup>1</sup>H-, <sup>2</sup>H-, <sup>13</sup>C-1D, <sup>1</sup>H-Spin Diffusion, <sup>1</sup>H-2D exchange, 2D WISE) show a mobile interface and a relative rigid polymer even at high solid contents >95%. Depending on the surfactant (e. g. poly(ethylene oxide) surfactants) and copolymer (sodium ethylene sulfonate) system a swelling and mobilisation of the polymer in the interface was found. The size and distribution at the polymer-water interface of these surfactants and different copolymers resulted in characteristic effects on the film formation process. The spectra showed changes in the dynamics of the studied latex systems.

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## 29.A2

## STRUCTURE FORMATION IN HETERO PHASE POLYMERIZATION

D.N. Yemelyanov, I.E. Smetanina

*Chemistry Institute, Nizhny Novgorod State University, Nizhny Novgorod, Russia*

The study results of structure-rheological properties of reaction masses in heterophase (precipitation) polymerization of some vinyl monomers and of their models were generalized.

Under conditions of the heterophase polymerization at small conversions there forms a free dispersed system in which globular polymer particles isolating from the reaction system act as a dispersed phase (a viscous-newtonian system). With increasing the concentration of the dispersed phase the particles interact and their aggregation followed by the formation of separate network elements occurs. This reaction mass is a liquid-plastic system characterized by a low critical shearing stress and a weak anomaly of viscosity. The polymerizate structure is totally thixotropic (a structure-viscous dispersion).

A further polymerization results in the increase of contacts of dispersed phase particles and the appearance of a dense network that leads to the formation of a bonded-disperse system. Its rheological behavior is governed by the character of the dispersion medium (the degree of aggregative and kinetic stability of the system). If the dispersion medium has individual interacting macromolecular coils the reaction system is a structure-viscous dispersion with a pronounced ultimate strength. If in the dispersion medium the network of macromolecular or structural "catchings" is formed, the reaction mass is a gel characterized by considerable elastic strains. At final degrees of conversion the system transforms into a structure-brittle state. The end product is a brittle body with a high modulus of elasticity and strength, and it shows no flow.

## 30.A3

## STABILIZATION OF FOAMS BY POLYETHYLENGLICOL-CETYLPYRIDINIUM BROMIDE MIXTURES

Aidarova S.B., Musabekov K., Nicolaeva N.

*Kazakh State National University, Almaty, Kazakhstan*

One of actual problem of modern colloid chemistry is stabilization of foams. This problem can be decided by investigation of foams and thin films properties. Results of investigation the influence of polyethyleneglicol (PEG) on stability and capillary pressure in Gibbs-Plato channels of foams, generated from water solutions of cetylpyridinium bromide (CPB), are represented in this work.

It was showed, that foamforming ability of PEG-CPB mixtures depends from  $n=[CPB]/[PEG]$  ratios. At lower significances of  $n$  foam formation is lowly. At higher  $n$  foam formation and capillary pressure in Gibbs-Plato channels higher.

The influence of molecular weight of PEG and pH on stability of foams, generated from water solutions of CPB, are investigated. Very stable foams can be produced with PEG, which have a molecular weight roov and on  $pH=3$ . This phenomena can be explained by low significances of surface tension and high significance of surface viscosity.

So, the properties of foams, stabilized with PEG-CPB mixtures, can be regulated by regulation of molecular weight of PEG, pH and molar ratio of  $[CPB]/[PEG]=n$ .

## 31.A3

## PHYSICS OF FOAM PATTERNING IN POROUS MEDIA

A.Bazilevsky<sup>1</sup>, K.Kornev<sup>1</sup>, V.Mourzenko<sup>1</sup>, A.Rozhkov<sup>1</sup> and G.Shugai<sup>2</sup><sup>1</sup>*The Institute for Problems in Mechanics, Russian Academy of Sciences, Moscow, Russia*<sup>2</sup>*Royal Institute of Technology, Stockholm, Sweden*

The problem of foam distribution in porous media excites interest due to wide applications of foams in different technologies, oil and gas recovery, waste management, medicine are only few of them (Hanssen, 1992; Kovscek and Radke, 1994). It is found (Hanssen, 1992; Kovscek and Radke, 1994) that a foam-saturated sample can withstand a finite pressure differential in the absence of motion, if all active channels are blocked by foam lamellae. This issue is of interest for better understanding of initial penetration of the externally applied pressure difference into a porous sample saturated by gas and foam. If compressibility of the gas in bubbles is not accounted for, to increase the pressure by a factor of  $\Delta p$  in a sample with macroscale  $L$ , it is required to overcome the huge capillary barrier  $\Delta p \sim \sigma L/r^2$ , where  $\sigma$  is the surface tension and  $r$  is the pore size. The experimental values are essential lower than this estimate. It turns out that allowance for the gas compressibility offer a clearer view of how the capillary barrier is broken. Notice, that the mathematical statement of the problem is close to that of the problem of the critical field determination for vortex creation in Josephson superconductor (Hansen and Lindelof, 1984; Kornev, 1995). We consider the 1D model of foam in porous medium as a bubble chain confined in capillary with wavy crosssectional area. Thermodynamics of both individual lamella and ensemble dictates the fate of the bubble train under a load. The disjoining pressure of wetting films also plays a role in appearing the up-to-start critical pressure drop. Some experimental support of this assertion will be presented. Mathematically the model of bubble train patterning is close to the Ulam mapping (Lichtenberg and Lieberman, 1983) and the problem of determination of the up-to-start pressure drop is reduced to analysis of transition of regular regime to chaotic regime for this mapping. Making use the computer experiment based on the theory of dynamic system we find the critical pressure drop as a function of input parameters such as surface tension, gas compressibility and number of lamellae in train. Conditions for transition from periodic to glass-like distributions of foam lamellae is found and comparison with existing experimental data is presented.

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### 32.A3 DEFINITION OF THE STABLE FORM OF A HYPOTHETICAL STABLE CELL AND DIFFUSION IN POLYHEDRAL FOAMS

S.E.Bochenkov and A.V.Pertsov

*Chemistry Department, Moscow State University, Moscow, Russia.*

The approach analogous to that of von Neumann for 2D foams [1] was applied to 3D case. It was shown that in polyhedral foams the total surface of any cell changes proportionally to time ( $dS/dt = \text{const}$ ), where the constant depends only on number of faces and vertices of the cell, that is, on its form, and can be calculated theoretically. The result is:

$$\frac{dS}{dt} \approx 8qB(kV - F)$$

where V and F - number of vertices and faces, correspondingly;  $k=0.59$ ;  $q = \bar{R} \frac{dS/d\bar{R}}{dV/d\bar{R}}$  - coefficient of cell form which does not depends on time (e.g., for pentadodecahedron  $q=2.15$ , for cube  $q=3.46$ ),  $\bar{R}$  - is the mean radius of the sphere which the cell;  $B = (\pi\sigma D)/h$ , where  $\sigma$  - surface tension of the solution, D - diffusivity of gas in the cells,  $h \sim \text{const}$  - film thickness.

It is possible to find the form of so called *critical cell*, that is, the cell which does not change its volume in time, comparing  $dS/dt$  to zero. Thus one can obtain the following values:

$$F=13.40, V=22.79, E=34.19,$$

where E is the number of cell edges. Calculated figures are in a good agreement with experimental results of Matzke [2], although in the original theoretical calculation of the same values made by Schwarz [3] a misprint had been admitted, which was repeated later in the monography [4].

Finally, the attempts of calculation of distribution of foam cells in time and form due to gas diffusion between cells were made.

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### 33.A3 DIFFUSING WAVE SPECTROSCOPY OF FLOWING FOAM

J.C. Earnshaw and J. Uhomobhi

*The Department of Pure and Applied Physics, The Queen's University of Belfast,  
Belfast BT7 1NN Northern Ireland*

Diffusing-wave spectroscopy has been used to study the effects of strain upon the dynamics of a model foam (shaving-cream). The observed data exhibit two time scales, one slow and the other rather faster. The behaviour of the latter quasi-exponential feature is consistent with the hypothesis that the relevant dynamic process reflected in the light scattering involves local rearrangement events in the foam [1]. The slower component in the data appears to arise from plug flow in the foam, and is physically less interesting.

The rate of rearrangement events underlying the fast component is increased in strained foam [2]. Above a threshold strain the rate at which elementary strain-induced rearrangements occur in the foam is



proportional to strain rate [3]. These results are in accord with the findings of recent computer simulations. However, below a threshold strain rate the rate at which elementary strain-induced rearrangements occur depends only on the strain [4], whereas it is above this threshold that the rate is proportional to strain rate. A possible mechanism for the unexpected behaviour at low strain rates is outlined.

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### 34.A3 ROLE OF THE STRUCTURAL-MECHANICAL BARRIER FORMED BY GELATIN-CETYLPYRIDINIUM CHLORIDE COMPLEX IN FOAM STABILITY

V.N. Izmailova<sup>1</sup>, S.R. Derkach<sup>2</sup>, G.P. Yampolskaya<sup>1</sup>, V.N. Chernin<sup>3</sup>

<sup>1</sup>Moscow State University, Moscow, Russia

<sup>2</sup>Murmansk State Technical University, Murmansk, Russia

<sup>3</sup>NPAO "Sintez PAV", Shebekino, Russia

Ability of complexes formed gelatin and low-molecular-mass surfactant to foam stabilization was studied.

It was shown mixtures of gelatin and surfactant in aqueous solution give rise of the surface active complexes. The properties of these complexes are not additive to individual components ones. These data give possibility to use the complex formation to enhance the disperse systems stability in particular foam.

The work has been aimed to study the stability of the concentrated bubbled foams and the models of foams - thin foam films stabilized by gelatin-cetylpyridinium chloride complex. Kinetic rate constants ( $k$ ) of foam coalescence and effective activation energies of the coalescence process ( $E$ ) have been determined. Depending on the ratio of the components in the gelatin-surfactant system  $k$  varies from  $5 \cdot 10^{-5}$  to  $1.5 \cdot 10^{-3} \text{ s}^{-1}$ ,  $E$  values are from 25 to 30 kJ/mol.

Thin films (elements of foam) were studied by a microinterference method. Diagram of the films stability depends on the component concentrations. Tension ( $\Delta$ ) of the black films was  $8 \cdot 10^{-3} \text{ mN/m}$  where  $\Delta = 2 \cdot (\sigma^l - \sigma^f)$ ,  $\sigma^l$  - surface tension,  $\sigma^f$  - film tension.

Rheological parameters of the foam macroscopic films were measured using the method of progressively increased load and attenuated oscillation. When the foam stability is a maximum the films are characterized by high values of the rheological parameters: viscosity is 80 mN\*s/m, yield shearing stress is 40 mN/m, elasticity modulus is 10 mN/m.

Under such condition adsorption layers are characterized by surface parameters: surface tension is 35 mN/m, viscosity is 150 mN\*s/m, yield shearing stress is 3 mN/m, elasticity modulus is 4 mN/m.

Hence, the special structural-rheological properties of adsorption layers and thin foam films cause enhanced foaming and stabilizing ability of the gelatin-surfactant complexes.

### 35.A3 EFFECT OF MOTION ON BUBBLES LIFETIME AT SOLUTION SURFACE

B. Jachimska, P. Warszynski and K. Malysa

*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Cracow, Poland*

Foam are formed under dynamic non-equilibrium conditions and therefore their properties, especially during formation and first moments of existence, may not be determined by and do not need to be directly related to their equilibrium quantities. Every disturbed system needs same time to re-establish its surface coverages and this "relaxation" time can differ by orders of magnitude for various systems. Formation of any foam system can be considered as consisting of: i) dispersion of gas phase into bubbles, ii) motion of bubbles in solution towards solution/gas interface, and iii) formation of a mono- and multilayer foam. The processes occurring in solution during bubble formation and motion towards the interface can have an important influence on properties of the foam formed, especially in the case of transient, short-time

living foams. Every motion, if quick enough, leads to disequilibrium of surface coverages over surface of moving bubble.

The paper presents results showing that motion of bubbles in n-butanol and n-nonanol solutions leads to disequilibrium of the surfactant coverages over the bubble surface. Average lifetimes of single bubbles at free solution surface located far and close to the point of the bubbles formation (capillary orifice) were determined. When the solution surface was located far from the capillary, the viscous drag of fluid acting on the moving bubble interface should result in creating at the upstream pole of the moving bubble non-equilibrium adsorption coverages, much lower than the equilibrium ones. On the other hand in the case when the solution surface was close to the point of bubble formation, the motion induced disequilibrium of the bubble coverage should be much smaller. Differences in the adsorption coverages at the top pole of the moving bubble should reflect in the bubble lifetime. The bubble lifetime at the solution surface close to the point of formation should be longer because the bubble adsorption coverage will be closer to the equilibrium one. For every location of the free surface, lifetime of at least 100 single bubbles were measured to obtain a value of the average lifetime for a given solution concentration. It was found that the average lifetimes  $t_{av}$ , of bubbles at the solution surface located far away were shorter than at the solution surface situated close to the point of the bubble formation. For examples for n-butanol solution of concentration  $1.5 \times 10^{-2}$  M, the appropriate values were  $t_{av} \text{ far} = 6\text{s}$  and  $t_{av} \text{ close} = 23,5\text{s}$ , respectively. It shows that the bubbles with nonequilibrium coverages arrived to the solution surface located far away and as a result of it asymmetrical foam films were formed and their stability was lower than the symmetrical ones.

### 36.A3 THE ISOELECTRIC STATE AT THE SOLUTION/AIR INTERFACE- EFFECT ON THE STABILITY OF FOAMS AND FOAM FILMS FROM NONIONIC SURFACTANTS

**Kh. Khristov, D. Exerowa, R. Yankov**

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Model studies of foams and single foam films under close and defined conditions are employed to study the effect of the isoelectric state ( $\text{pH}^*$ ) at the solution/air interface on the stability (lifetime) of foams from tetraethyleneglycol monodecyl ether  $\text{C}_{10}(\text{EO})_4$  and eicosaoxy-ethylene nonylphenol ether, NP20. The parameter  $\text{pH}^*$  and the potential of the diffuse electric layer  $\phi_0$  are found by the method of the equilibrium foam film. A metastable zone in which films are both equilibrium and rupturing, is established to appear at pH values higher than  $\text{pH}^*$ . Isotherms of disjoining pressure  $\Pi(h)$  are measured for the first time at different pH and its influence on the interaction forces in the foam film is revealed. At constant solution ionic strength the pH change affects strongly the pressure at which films rupture. However, at equal ionic strength and surfactant concentration, the stability of foams dramatically decreases when  $\text{pH}^*$  is reached.

### 37.A3 CRITICAL PRESSURE OF DESTRUCTION OF FOAMS AND SINGLE FOAM FILMS: EFFECT OF FILM SIZE

**Khr. Khristov and D. Exerowa**

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The Foam Pressure Drop and the Thin Liquid Film Pressure Balance Techniques are used to study foams and single foam films stabilized either by NaDoS or amphiphile polymers. A pressure is reached at which the free films rupture and the foam destruct very fast (avalanche-like). We named these critical pressure ( $\Delta p_{cr, \text{film}}$ ) of film rupture and critical pressure of foam destruction ( $\Delta p_{cr, \text{foam}}$ ), respectively. Their values depend on the surfactant kind and on the type of foam films (common thin, CBF and NBF). Below 20 kPa, the pressures  $\Delta p_{cr, \text{film}}$  and  $\Delta p_{cr, \text{foam}}$  are equilibrium and close by value for single foam films and foams from the same amphiphile solution. However, depending on the surfactant kind there appears a significant difference when their critical values is higher. The  $\Delta p_{cr, \text{film}}$  vs. film size dependences as well as  $\Delta p_{cr, \text{foam}}$  vs. foam dispersity indicate that the film size and foam dispersity, respectively, strongly affects the critical

values. The histograms of film size distribution reveal that the foam always contains films that are of a larger than the average size. They rupture at the lowest pressures and initiate the destruction of the whole foam. This is a possible explanation of the difference observed between  $\Delta p_{cr, film}$  and  $\Delta p_{cr, foam}$  values.

### 38.A3 FOAM FROM ABA BLOCK COPOLYMERS AQUEOUS SOLUTIONS

**Khr. Khristov and D. Exerowa**

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The role of foam films in the stability and drainage of foams from ABA block co-polymers is considered. The Foam Pressure Drop Technique which involves applying an increased and controlled pressure in the foam liquid phase makes it possible to estimate this role under strictly defined conditions: capillary pressure, type and size of foam films, etc. The  $\Pi(h)$  isotherms of disjoining pressure measured for single foam films under conditions close to those in foam clarify the influence of the type of foam films: common thin films and films without electrostatic component of disjoining pressure, on foam stability. The experiments are performed with the Thin Liquid Film-Pressure Balance Technique developed on the basis of the microinterferometric method of Sheludko-Exerowa. Foam lifetime vs. applied pressure ( $\tau_p/\Delta p$ ) functions along with the  $\Pi(h)$  isotherms indicate that the type of foam films (i.e. interaction forces acting in them) has a decisive role in the stability of foams. The kinetics of the foam drainage process shows that the initial slopes of the water content vs. time  $W(t)$  dependences characterising the rate of foam drainage is determined also by the type of foam films in the foam.

### 39.A3 EFFECT OF SURFACE TANGENTIAL MOBILITY ON PLATEAU BORDER PROFILE DURING LIQUID FLOW THROUGH A FOAM UNDER PRESSURE DROPS

**P.M. Kruglyakov and N.G. Vilkova**

*State Academy of Architecture and Building, Penza, Russia*

The profile of Plateau border radius of curvature ( $r$ ) along the foam column height ( $l$ ) during liquid flow through a foam under a pressure drop (assuming that border surfaces are immobile) and the experimental border profiles were obtained earlier for foam with the different type of the foam films (P.M. Kruglyakov, L.L. Kuznetsova, 1982 and N.G. Fokina, P.M. Kruglyakov, 1986).

In this work the correction was introduced into the equation for the volume rate of flow under the influence of pressure drops. This correction takes into account the border surface mobility by the method of Desai and Kumar (1982). Introduction of the border surface mobility correction leads to the linear dependence of  $(r^3 + kr^{3.5})$  on foam height (here  $k = 1.98 * (\eta/\eta_s)^{0.5}$ ,  $\eta_s$  - the surface viscosity,  $\eta$  - the dynamic viscosity of bulk liquid).

It was established that in the foam from the mixture of sodium dodecylsulfate and gelatine the experimental radii were less than theoretical ones obtained with the surface viscosity taken into account.

For instance the experimental and theoretical Plateau-Gibbs border radii were  $6.8 * 10^{-4}$  cm;  $18 * 10^{-4}$  cm and  $8.5 * 10^{-4}$  cm;  $23.9 * 10^{-4}$  cm in the middle part of the Plateau-Gibbs border for the 2cm height of foam from sodium dodecylsulfate and from dodecylsulfate with gelatine addition respectively.

## 40.A3

STABILITY AND DRAINAGE OF POLYHEDRAL FOAMS:  
RECENT ACHIEVEMENTSP.M. Kruglyakov<sup>1</sup>, Khr. Khristov<sup>2</sup> and D. Exerowa<sup>2</sup><sup>1</sup>*State Academy of Architecture and Building, Penza, Russia*<sup>2</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

A significant progress in the study of foams from aqueous surfactant solutions has been achieved during the last years applying the Foam Pressure Drop Technique, developed by us for investigation of foams and Thin Liquid Film-Pressure Balance Technique for investigation of single foam films. The advantages of these complimentary techniques involve performing experiments with foam and single foam films under similar and well defined conditions. The effect of foam film type (i.e. surface forces acting in them) on the stability and drainage of polyhedral foams is analysed. Results from the study of stationary liquid flow through the foam under gravity and at pressure drop are discussed with respect to: border profile, flow rate dependence on Plateau border radius, foam film type, surface and dynamic viscosity. Non-stationary drainage is discussed with respect to: kinetics of pressure establishing in the foam liquid phase, rate of liquid flowout and the maximum "excess" pressure in the foam.

The influence of capillary pressure on the destruction rate of foam column, the concept of critical disjoining pressure and the techniques for the study of polyhedral foams are also considered.

## 41.A3

RESEARCH OF NON-EQUILIBRIUM EFFECTS OF FOAM  
IN A POROUS MEDIUM

A. Latypov, R. Bakhtizin

*Ufa State Petroleum Technological University, Ufa, Russia*

In recent years foam application there are highly concentrated gas emulsions in solution, stabilized surfactants have been widely used in gas production industry. Such important problems as oil-gas recovery increase, underground gas storage intensification can be effectively solved by using foam due to their specific rheological properties. These properties are specified by instability phenomena on the surface of elastic bubbles which constitute foam in the presence of surfactant molecules. Experimental researches indicate that instability of sorption processes in the foam results to great hydrodynamic instability of the foam especially in filtration processes.

Foam hydrodynamic instability in the porous medium results to kinetic effects of retardation-relaxation of filtration and pressure velocity which have a great influence on the efficiency of various technological processes of foam application in the porous media.

Similar to Maxwell model viscoelastic model of rheological behaviour of the foam in the porous medium has been proposed according to the results of experimental researches with foaming agents Prevotcell-WON, WOF, OP-10, OP-45, Stenol-100, OS-10. We can explain phenomena of unsteady creeping of the foam in the porous medium, pressure relaxations by the application of the proposed model.

Technological methods have been developed to direct instability properties of the foam in the porous medium allowing to regulate properties of the system in the desired way.

## 42.A3

## STRUCTURE OF FOAMS PRODUCED BY AGITATION

P. Licinio and J.M. Figueiredo

*Dep. de Física - Universidade Federal de Minas Gerais - Belo Horizonte - Brasil*

Liquid foams are non-equilibrium structures and, once formed, coarsen with time until vanishing. Much work on foams has centred on determination of these asymptotic structures. Here we present an investigation of structures obtained prior to the quasi-equilibrium coarsening, i.e. immediately after foam creation by agitation. We produced three dimensional foams by mixing air and water + Extran solutions in a

shaker under different agitation conditions (frequency, symmetry and test tube fillings). Long time observations revealed that bubble radius distributions become stationary. Differently from the maximum-entropy coarsened distributions for 2D foams, we found radius distributions to be Gaussian for strong agitation conditions. The stationary distributions are found above a threshold shaking energy. Foams created at the threshold store finite energy which increases roughly linearly with applied energy.

### 43.A3 INVESTIGATIONS OF FOAM LAMELLA STABILITY AND THE AMPHIPHILES' MOLECULAR GEOMETRY

K. Lunkenheimer<sup>1</sup>, K.-D. Wantke<sup>1</sup>, K. Malysa<sup>2</sup>

<sup>1</sup>Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5,  
D-12489 Berlin, Germany

<sup>2</sup>Institute of Catalysis and Surface Chemistry, ul. Niezapominajek 1, PL-30239 Cracow, Poland

Generally a foam represents a highly complex system which still lacks a general theory on foam stability. To find out under which conditions certain parameters are decisive for stabilizing a foam system we have looked for an appropriate experiment which enable the physical conditions as well as the chemical system to be as simple as possible.

Hence we have chosen two nonionic amphiphiles (n-decyldimethylphosphine oxide [I] and tri-n-butyl phosphine oxide [II]) which are advantageous stabilizers in various respects because of the following facts:

- i) They are chemically very stable;
- ii) Their chemical structure consists of an identical polar group and identical number of carbon atoms. Thus, the two structures' different foamability should mainly be attributable to differences in their molecular geometry.
- iii) They reveal ideal surface behaviour.

Foam lamella stability was determined in a rectangular glass frame.

The adsorption parameters reveal pronounced differences in the amphiphiles' cross sectional areas. The surface area demand of species II with bulkier head group is by 75 % larger than that one of species I.

Experimentally it was found that the lamella life times  $\tau$  of the two systems are very different. The bulkier amphiphile's (II) lifetime is smaller by one order of magnitude. Although the lamella life times are greater by orders of magnitude than the equilibrium adsorption time,  $t_{eq}$ , a linear relationship between  $\tau$  and the logarithm of the Marangonic elasticity modulus EM was found for each species. However, in comparing the lamellae at the same, relative surface state we succeeded in describing the foam lamella stabilities by the amphiphiles' adsorption data only.

Thus, as amphiphiles with rather large cross sectional areas can produce only comparatively low surface elasticity this will result in smaller foam lamella stability.

These results are discussed with respect to the mechanism of foam stabilizing as well as to applications in monitoring and optimizing foam systems.

### 44.A3 RAMAN STUDIES OF THREE-DIMENSIONAL FOAM

Zh.S. Nickolov and N. Goutev

Department of Quantum Electronics, Faculty of Physics, Sofia University, 5, J. Bourchier Bul.,  
1164 Sofia, Bulgaria

The structure of the thin liquid films in a stable three-dimensional foam (shaving cream) has been studied by Raman scattering [1]. Two phases existing in the foam films are identified - lamellar and isotropic. The lamellar phase is an ordered multilayer structure (gel) of stearic acid molecules in all-trans conformation. This is proved by the shape of the Raman spectra in the C-H stretching region and by the values of a characteristic parameter determined from them - the intensity ratio R. The spectra in the C-C stretching and C-H bending regions support this conclusion as they show absence of features characteristic

of gauche conformations. An analysis of the Raman spectra in the C-H bending and C-H stretching regions suggests that stearic acid molecules in the foam lamellar phase have a hexagonal packing.

On the basis of Raman spectroscopic data we propose a model of foam molecular structure and its evolution. According to it small bilayer lamellae dispersed in the foam films after foam formation gradually self-organize around the bubbles in large shell-like bilayer structures. This arrangements is induced initially by the gas-liquid interfaces of the bubbles and consequently by the interfaces of the bilayer structures with the foam liquid. The process of organization of small lamellae into large bilayer structures can be followed by changes in the intensity ratio  $R$  of C-H band and in the halfwidth of antisymmetric C-H stretching fundamental  $d^+$ .

The investigations carried out in this work demonstrate the capabilities of Raman spectroscopy to study the microstructure of three-dimensional foams and its dynamics. Raman spectroscopic studies can be employed to study ageing of foams on the molecular level and can be possibly extended to characterization of factors affecting foam stability.

I. N. Goutev and Zh.S. Nikolov, *Physical Review E*, 54, 1725 (1996)

## 45.A3

### MODELLING THE STRUCTURE AND PROPERTIES OF THREE-DIMENSIONAL FOAM

R. Phelan and D. Weaire

*Physics Department, Trinity College, Dublin, Ireland*

The rapidly expanding field of 'soft matter' encompasses such materials as foams, emulsions, gels, polymers and liquid crystals. Foams in particular are experimentally accessible and bring together many of the essential elements of such materials combining geometry, fluid mechanics, structure dependent rheology, etc. We outline some of the recent work of the theory group at TCD on the computational modelling of foam structure and physical properties.

A foam is a two phase system consisting of gas bubbles or cells in a liquid, separated by thin films wherever they contact each other.

Two-dimensional foams have long been a focus for the simulation work of the theory group at Trinity College Dublin, (e.g. Hutzler *et al.* (1995)). More recently we have tackled the case of three-dimensions which presents particularly demanding computational difficulties.

Using software developed in the United States (Brakke 1992), we have undertaken a study of foam structure and properties. Our initial work established an ideal structure for dry monodisperse foam (one for which the liquid content is negligible and where the bubbles have equal volume), (Weaire and Phelan 1994). We have since extended our methods to include foams of finite liquid content (Phelan *et al.* 1995) and have examined rival bulk structures and their stabilities as a function of liquid fraction.

Foam samples trapped between flat glass plates or cylinders present interesting and complex ordering phenomena. In parallel with experimental work we have begun to analyse these ordering effects.

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## 46.A3 TEMPERATURE DEPENDENCE OF THE FOAM DESTRUCTION PREPARED FROM THE N-DODECYLOXYMETHYLPYRIDINIUM CHLORIDE SOLUTION

E.V. Porodenko, A.V. Pertsov

*Department of Chemistry, Moscow Lomonosov State University, Moscow, Russia*

The internal destruction of foams causes the increase of the cells' dimension. Usually this process is implemented by two mechanisms: either by coalescence of foam cells or by gas diffusion via foam's films from the smaller cell to the bigger one. In the present work we have investigated the internal destruction of foams bubbled from the aqueous solution of N-dodecyloxymethylpyridinium chloride in the temperature range of 291-333 K, where the concentration of solution was  $10^{-2}$  M. The influence of temperature on the rate of the internal destruction of foams was investigated experimentally as the  $K(t)$  dependence, where  $K$  is the expansion factor,  $t$  - time. It has been found out that under chosen conditions foams were stable with high expansion factor ( $K > 200$ ), all of the foams reached the hydrostatic-equilibrium state. That's why we considered that coalescence was the main mechanism of the destruction of foams. The time of foam destruction ( $t_d$ ) at given temperature and the effective activation energy ( $E_{eff}$ ) were chosen as characteristics of the process, where  $t_d$  is inversely proportional to the rate constant of the process. The value of  $E_{eff}$  is calculated from the temperature dependence of  $t_d$ . It was shown that at the rate of the foam destruction grew with the temperature increased. The statistically calculated value of  $E_{eff}$  equals  $53,8 \pm 7.1$  kJ/mol. The obtained value of  $E_{eff}$  is in a good agreement with the literature characteristics of the nucleation process of a vacancy (hole) in the bilayer film.

## 47.A3 THE EFFECT OF MELAMINE ON THE FOAM KINETICS OF POLYURETHANE MODEL SYSTEM. THE EFFECT OF MELAMINE PARTICLES ON FILM FORMATION

N. Sándor<sup>1</sup>, E. Geladé<sup>2</sup>, R. van Maris<sup>3</sup> and Gy. Rácz<sup>1</sup>

<sup>1</sup>*Department of Physical Chemistry, Technical University of Budapest, 1521 Budapest, Hungary*

<sup>2</sup>*DSM Research P. O. Box 18, Geleen, The Netherlands*

<sup>3</sup>*DSM Melamine P. O. Box 27, Geleen, The Netherlands*

The stability of foams can be investigated by single foam films representing many of the foam characteristics. The liquid films thin as the result of capillary and gravitational forces. Thinning takes place by laminar flow and/or turbulent motion. The drainage of aqueous mobile films can easily be studied by interference experiments.

In the recent years the investigation of high viscous systems, like foaming properties, adsorption and diffusion process of surfactants of large molecular weight in viscous solvent, has become important parallel with the increasing interest of polymeric foams.

Flexible polyurethane foams are used in seating and bedding, therefore their flame retardancy must be a necessary characteristics. Melamine, in the form of solid particles, has been found a sufficient flame retardant. It is well known from literature that solids influence the stability of foams. In our work the effect of melamine particles on the film formation is studied in a polyurethane model system (polyol, surfactant, melamine).

Interference experiments could not be used because of the large viscosity resulting slow drainage. The presence of particles gives the possibility to observe the flows in the film. In this way the complete circulation can be followed. The films of the model system have been found mobile films showing marginal regeneration. The mentioned flows and their rates are discussed.

Film formation was combined with surface tension measurements on the pool surface. Previously it was shown experimentally, that the rate of surfactant adsorption is very slow from diluted solutions, thus in the case of films drawn from those solutions the adsorption can be neglected, and the rate of surface diffusion can be investigated.

The changes in the surface tension of the pool were measured and the moles of surfactant diffused from the surface of the pool to the surface of the film were calculated. This quantity was found to be a few

per cent of the moles necessary for equilibrium coverage. The low rate of surface diffusion showed that the fresh film surface is nearly independent on the pool surface and the meniscus behaves as a slit producing a film with nearly surfactant free surface.

The effect of surfactant and melamine concentration is discussed.

Two characteristic phenomena were observed during film formation from suspension containing 25 pphp melamine ultra fine.

1. The convective currents are slower in the melamine filled film than in the corresponding melamine free lamellae. This may be mainly caused by the increased viscosity.

2. No surface tension difference was seen on the surface of the pool after film formation. It seems that the melamine hinders the surface diffusion.

## 48.A3

### STABILITY OF NONAQUEOUS TRANSIENT FOAMS: SYSTEM AMPHIPHILE $C_mE_n$ + n-ALKANE

Luis M. Trejo<sup>1</sup> and Bengt Kronberg<sup>2</sup>

<sup>1</sup>Laboratorio de Termofísica, Facultad de Química, U.N.A.M., Mexico, D.F. 04510 Mexico.

<sup>2</sup>Institute for Surface Chemistry, Box 5607, Stockholm S-114 86 Sweden.

We studied the transient foam formed in nonaqueous binary systems by some polyethyleneglycol monoalkyl ethers of the type  $C_mE_n$  with  $m \leq 6$  and  $n = 1, 2$  or  $3$  mixed in different n-alkanes, mainly n-hexadecane. We measured the solubility, surface tension and transient foam stability of several  $C_mE_n$  + n-alkane systems as a function of mole fraction  $X$  and temperature. The surface tension  $\sigma$  was obtained using the maximum bubble pressure method with a Sensadyne 6000 equipment. The transient foam stability was measured in a jacketed cylindrical glass cell with 2.5 cm of diameter and 30 cm of length with a fitted glass of porosity 2 (pore size 40-100  $\mu\text{m}$ ) at the bottom: Foam stabilities  $\Sigma$  were obtained from the slope of the plot volume of transient foam formed as a function of nitrogen gas flow, working in the interval below 100  $\text{cm}^3/\text{min}$ . The curves  $\sigma$  vs  $X$  obtained: i) show negative deviations to the ideal behavior which become larger on increasing the difference on surface tensions of the pure components and ii) present a horizontal inflection at the critical composition close to phase separation, as reported previously by others authors. The curves  $\Sigma$  vs  $X$  measured show a maximum at the critical composition which is enhanced close to phase separation, in similar way as the surface compositions  $\Gamma$  calculated with the surface tensions and using the regular solution theory. Having in mind that the alkane is the component with lower surface tensions of the system, these results support the ideas that the surface activity of a component is primarily due to its weak interaction with the other component, so a tendency to phase separation is a general indicator of surface activity and therefore more stable transient foams are formed.

## 49.A3

### RELATION BETWEEN SURFACE PROPERTIES AND OSTWALD RIPENING IN AQUEOUS FOAMS

H.K.A.I. van Kalsbeek<sup>1</sup>, G.A. van Aken<sup>2</sup> and A.Prins<sup>1</sup>

<sup>1</sup>Wageningen Agricultural University, Department of Food Science Division of Integrated Food Technology and Food Physics, Wageningen, The Netherlands

<sup>2</sup>Netherlands Institute for Dairy Research, Department of Technology, Ede, The Netherlands

Ostwald ripening or disproportionation is one of the most important factors in the stability of aqueous foams. Ostwald ripening is the coarsening of foams by gas transfer from smaller bubbles to bigger ones. The transport is caused by the higher Laplace pressure difference in the smaller bubble. As a result of this the solubility close to the smaller bubble is higher than close to the bigger bubble. This causes gas to transfer from the smaller to the bigger bubble.

The rate of dissolution of a bubble in a liquid is affected by the surface properties of the bubble surface. During the shrinking of a bubble the surface is compressed and if the adsorbed surfactant does not



desorb during this compression, the adsorbed amount will become higher and the surface tension may decrease. This decrease of the surface tension is however dependent on the surface properties.

Proteins usually have a high affinity for adsorption at surfaces and proteins do usually not desorb once they are adsorbed. On the other hand the adsorption process of low-molecular weight surfactants like soaps is usually more reversible. As a result it is thought that soaps will desorb much easier during compression of the surface than proteins and hence proteins are more able to decrease the surface tension during compression.

To describe this decrease in surface tension, the surface dilational viscosity ( $\eta_s^d$ ) can be used, which is given by:

$$\eta_s^d = \frac{\gamma_{ev} - \gamma_{comp}}{d \ln A / dt}$$

in which  $\gamma_{ev}$  is the equilibrium surface tension,  $\gamma_{comp}$  is the surface tension in compression and  $\gamma_{comp}$  is the relative rate of compression of the surface.

It is found that  $\eta_s^d$  for protein solutions ( $\beta$ -casein,  $\beta$ -lactoglobulin,  $\alpha$ -lactalbumin) is about an order of magnitude higher than for a soap solution- (Sodium Lauryl Sulphate). It is also found that the dissolution rate of a bubble stabilised by Sodium Lauryl Sulphate is higher than the dissolution rate of a protein stabilised bubble. Hence, Ostwald ripening of foam stabilised by Sodium Lauryl Sulphate proceeds faster than in the case of protein stabilised foam.

This shows that the surface dilational viscosity in compression is a good measure for the ability of a system to slow down Ostwald ripening in foam.

### 50.A3

#### INTERACTION OF SHOCK WAVES WITH AQUEOUS FOAMS AND GAS-DROPS MEDIA

**E.I. Vasiliev, V.A. Levin, S.Yu. Mitichkin, A.V. Pertsov, V.G. Testov, Hu Haibo**  
*Institute of Mechanics of the Lomonosov Moscow State University, Moscow, Russia*

Our researches have shown that even in weak shock waves, when the incident shock wave Mach number  $M > 1.2$ , aqueous foam behind the shock wave front is destroyed and gas-drop medium is formed. Present work contains the results of experiments and numerical simulation of the shock wave - aqueous foam layer interaction.

Experiments were conducted out in a vertical shock tube at  $1.05 < M < 1.5$  and average initial foam density  $4 < \rho_0, \text{ kg/m}^3 < 50$ . Features of pressure behaviour versus  $M$  and density distribution were studied. Simultaneous photographing of the foam destruction and gas-drop medium formation permitted us to explain the features of pressure wave.

For numerical simulation we used gas-drop theoretical model. It was supposed that the medium behind the shock wave front in foam is a mixture of gas, drops and droplets. The last are in equilibrium with the gas. The theoretical model takes into account surface destruction of drops in a gas flow behind the shock wave front, deposition of droplets onto drops, heat exchange between drops and the gas flow. Initial sizes of drops and droplets were defined on a basis of a developed model of foam and measurements of foam parameters changing in time. Gas dynamic equations were solved by a developed high accuracy modification of the Godunov's method.

The results of calculated pressure behaviour are in agreement with experimental one both in transmitted wave and in reflected from the shock tube end wall wave with tile exception of a relaxation zone after shock wave front immediately. Possibilities of the theoretical model improvement are discussed.

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### 51.A3 THE RELATIONSHIP BETWEEN FOAM STABILITY AND SURFACE RHEOLOGICAL PROPERTIES

Wantke, K.-D.<sup>1</sup>, Malysa, K.<sup>2</sup>, Fruhner, H.<sup>1</sup>, Lunkenheimer, K.<sup>1</sup>

<sup>1</sup>Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5,  
D- 12489 Berlin, Germany

<sup>2</sup>Institute of Catalysis and Surface Chemistry, 30239 Cracow, Poland

The stability of foams can be determined by measurements of the retention time  $t_r$ , which is defined as the average time necessary for a bubble to pass through the system consisting of a solution and foam. This is an appropriate method for investigation of special types of foams, e.g. for aqueous solutions of n-alkanols and of lower fatty acids, where the retention time has a characteristic dependence on the amphiphile's bulk concentration. The parameters of this function correlate with those of the adsorption isotherms of the solution concerned. This leads to a relation between foam stability and surface elasticity on the basis of a theoretical consideration. We have checked this relation by measurements of the surface elasticity of such systems with the oscillating bubble method. The results leads to some modifications of the relation for wetting foams.

In addition, more stable forms, e. g. a foam of a sodium dodecylsulfate solution, was investigated, and we could show that in general a rapid growth in the stability of foams correlates with an increase in the intrinsic surface viscosity of surfactant solutions. For such stable foam systems, the life time of a lamella was determined and compared with the results of the oscillating bubble measurements.

### 52.A3 THE PHYSICS OF FOAMS

D. Weaire

Department of Physics, Trinity College Dublin, Ireland

The physicist's ideal model of a soap froth has few ingredients: stable thin films enclose incompressible gas, and the surfaces of the films and Plateau borders have a constant surface tension. This minimal picture already offers rich and relevant properties. Steady progress has been made in determining these properties over the last decade or so. Computer simulations have played a key role, as have simple experiments. Most recently we have seen the extension of this work from two to three dimensions, and progress on the problem of drainage.

### 53.A4 ADSORPTION OF CETYLDIMETHYLBENZYLAMMONIUM CHLORIDE ON OCTANE-IN-WATER EMULSIONS IN THE PRESENCE OF TWEEN 80

Antonis Avranas, Vangelis Kamvisios, Irene Mandratzidou, Efi Malasidou

Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki,  
54006, Thessaloniki, Greece

The adsorption of the cationic surfactant cetildimethylbenzylammonium chloride (CDBACl) on the octane-in-water emulsion droplets was estimated and the adsorption isotherms were determined. The amount of CDBACl adsorbed was also measured in the presence of the nonionic surfactant Tween 80, below and above its critical micellar concentration. Various combinations were made concerning the time of the incorporation of the surfactants before and after the emulsification. The concentration of CDBACl on the emulsion droplets was higher when it is added before the emulsification without the nonionic surfactant. The adsorption of CDBACl on the surface of emulsion droplets when it was added prior to emulsification was shown to be almost unaltered by the presence of Tween 80. The addition of surfactants before emulsification resulted in a reduction in droplet size. The adsorption of CDBACl on the emulsion droplets was depended on their coverage by the molecules of Tween 80. In some cases a competitive adsorption of the emulsifiers for the oil droplet was observed leading to a displacement of surfactant molecules from the

interface. The adsorption isotherms were also determined by measuring the surface tension. The critical micelle concentrations of aqueous solutions of mixed surfactants had been determined and the adsorption parameters were calculated. The displacement of CDBACl from the emulsion droplets was broadly consistent with the interfacial tension data.

## 54.A4 EMULSIONS: FROM THEIR PREPARATION TO THEIR DESTRUCTION

**P. Bothorel**

*Centre de Recherche Paul Pascal (CRPP/CNRS) - F33600 Pessac, France*

From their preparation to their destabilization, emulsions raise a variety of challenging questions which are still far to be fully answered. Besides the empirical knowledge which is considerably widespread among the various specific applications, the basic understanding of emulsions is certainly progressing and we aim to give an overview of the most recent advances performed in our laboratory. We will focus particularly on the preparation of monodisperse emulsions, interdroplet forces and finally the coalescence process.

**Preparation of monodisperse emulsions:** A systematic exploration of emulsification through shear rupturing of droplets in complex fluids has been performed. Remarkably, a crude polydisperse emulsion can be ruptured into a monodisperse emulsion when a controlled shear is applied over a thin gap (less than 200  $\mu\text{m}$ ). The monodispersity becomes more pronounced when the premixed emulsion is viscoelastic and has a shear thinning viscosity. The direct production of monodisperse emulsions through droplet rupturing in viscoelastic fluids represents a new and well-controlled way of making colloidal fluid dispersions.

**Force measurements:** we have recently developed a direct measurement of colloidal forces between droplets by a technique involving magnetic fluids. This technique allows us to measure directly the pair force profiles between two droplets in the presence of any kind of surface active species that may adsorb at the oil-water interface.

**Coalescence:** Concentrated emulsions stabilized by non-ionic surfactants (type C12E5 or NP6) undergo coalescence when heated above a critical temperature. We observe a regime where coalescence leads to a unique droplet size (monodisperse emulsions) which continuously grows. In that regime, the evolution of the droplet radius  $R$  is governed by the empirical law  $dR/R^3 = w dt$ , where  $w$  is a constant frequency of coalescence per unit surface.  $w$  is related to the activation energy  $E_a$  that has to be overcome in order to produce a hole within the thin film separating two droplets. We study the influence of some experimental parameters (surface tension, droplet volume fraction, temperature) on the activation energy.

These works were done by J.Bibette, B.Deminiere, F.Leal-Calderon, T.Mason and O.Mondain-Monval in CRPP.

## 55.A4 THE PARTITION BEHAVE OF MIXED ANIONIC/NON-IONIC SURFACTANT

**Jiatai Bu, Wenhai Chen, Zhongxin Wen**

*Xinjiang Institute of Chemistry, Chinese Academy*

In this paper, the Partition behave between the toluene/water of mixed anionic/non-surfactant was investigated. As anionic surfactant we chosen alkyl sodium sulfonate, and as non-surfactant, we synthesized a series of block polymer of EO and PO which was initiated by  $^3\text{H}$  isotopic sample polyethylenepolyamin (AP). During our experiment we make all of the surfactant's concentration below them CMC. We measured the concentration of anionic surfactant in its aqueous by electrical conduction method, and determined the concentration of non-surfactant in its aqueous and its toluene solution by a liquid scintillation counting technique. The partition coefficient of surfactant between the toluene and water was determined when they as a pure surfactant solution and mixed surfactant solution respectively. See table 1 and table 2.

Table 1. The partition coefficient of non-surfactant AP

	HL B	Ko/w	K1o/w:AP with R <sub>12</sub> SO <sub>3</sub> Na	K2o/w:AP with R <sub>14</sub> SO <sub>3</sub> Na
AP 1	5.0	0.141	0.148	0.087
AP 2	8.0	0.221	0.196	0.204
AP 5	12.5	0.172	0.125	0.174
AP 8	14.5	0.096	10.056	0.0461

\*Ko/w is the partition coefficient of pure non-surfactant between toluene/water

Table 2. The Partition Coefficient of Alkyl sulfonate

	HLB	Ko/w	mixed with AP1	mixed with AP2	mixed with AP5	mixed with AP8
R <sub>12</sub> SO <sub>3</sub> Na	12.3	0.072	0.296	0.189	0.302	0.226
R <sub>14</sub> SO <sub>3</sub> Na	11.41	0.106	0.1212	0.017	0.059	0.032

As a result we see, about non-surfactant AP, the effective of alkyl sulfonate is not obvious and it's very different from salt effect. Alkyl sulfonate changed the HLB of the system and made the concentration of AP in water phase increase. But for the alkyl sulfonate, the effect of non-surfactant AP is more complex and obvious. The effect is related to the HLB of the non-surfactant AP. The interaction between alkyl sulfonate and AP existed, and we can determine the interaction constant if we complete more experiment in the future.

## 56.A4

### NMR MEASUREMENTS ON EMULSION STABILITY

Terence Cosgrove and Siân Calpin-Davies

School of Chemistry, University of Bristol, U.K.

Pulsed field gradient spin-echo experiments were performed on oil-in-water emulsions stabilised by a polymeric surfactant. The emulsions are highly concentrated with varying oil volume fractions from 10% to 50%. The data for a block co-polymer surfactant (PEO-PPO-PEO), shows that at low oil volume fractions the system is stable, but as the volume fraction is increased phase inversion occurs and the emulsion becomes a water-in-oil.

The NMR measurements were performed on a Jeol FX100 operating at 99.5 MHz. The gradient pulses are computer controlled and generated in the normal homospoil coils. The basic homospoil circuitry has been replaced by an Amcron M600 linear DC amplifier giving improved gradient strengths and stability. As part of the modification a separate control board was built to ensure a zero DC offset. Typically, a field gradient of 0.227 Tm<sup>-1</sup> has been achieved. The experiments were performed with a modified Hahn echo sequence (1). The surfactant solution was emulsified with toluene using a Silverson mixer for 5 minutes.

From the NMR data obtained we are able to determine the average oil droplet size, the degree of restricted mobility of the components and the free (bulk solution) to bound (adsorption at the liquid/liquid interface) surfactant ratio. From this information we can ascertain whether a particular emulsion is of the oil-in-water or the water-in-oil type and also measure the emulsions degradation. It has been observed that as the oil volume fraction is increased the system, that the degree of restriction of the oil passes through a region of instability, until at 50% oil volume fraction the system has phase inverted into a water-in-oil emulsion.

The bulk water phase at low oil volume fractions undergoes unrestricted diffusion, only slightly reduced due to the obstruction effects of the emulsion droplets (a route to measuring the volume fraction of

the droplets). At high oil volume fractions the water undergoes restricted diffusion characteristic of a water-in-oil emulsion.

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## 57.A4

### STABILITY OF MICRONSIZE EMULSIONS UNDER EQUILIBRIUM AND DYNAMIC CONDITIONS

Krassimir D. Danov and Ivan B. Ivanov

*Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry,  
University of Sofia, James Bourchier Avenue 1, Sofia 1126, Bulgaria*

The interdroplet interaction may lead even for very small drops to the formation of an intervening planar film. The formation of such film is determined by the interplay of the viscous forces and the other interactions: van der Waals, electrostatic, steric, depletion, etc. The role of different factors such as surface potential, electrolyte concentration, interfacial tension, micelles or small polymer molecules (which depending on the conditions may lead either to stratification, i.e. to stabilisation, or depletion, i.e. to destabilisation), droplet radius etc., on the film radius and the pair energy is studied.<sup>1</sup>

We have studied both theoretically and experimentally the role of surfactant on the life-time,  $\tau$ , of drops *with and without intervening film* in preequilibrated systems. When the surfactant is in the continuous phase  $\tau$  is determined mainly by the Gibbs elasticity of the interface and the disjoining pressure. When the surfactant is dissolved in the drop it has a minor effect on the life-time. Hence, the life times of emulsion drops depend primarily on the surfactant location. That is why the mere phase inversion may result in a change of the life-time by several orders of magnitude. The interfacial viscosity can be important for with high molecular surfactant such as proteins and/or for very small (micronsize) drops. We developed a theory of the drainage rate of very small films and a theory of the critical film thickness. Based on these results we formulated a new explanation and a quantitative theory of the Bancroft rule.<sup>2</sup>

With non-preequilibrated systems we studied three effects. When surfactant transfer *across the film surfaces* toward the drops takes place, the stabilisation is due to a spontaneous cyclic dimpling, which leads to the influx of liquid *inside the film* from the continuous phase. For surfactant transfer toward the continuous phase the emulsion films are stable due to a non-equilibrium osmotic pressure caused by micelle formation when the surfactant enters the continuous phase. Both effects strongly stabilise the system and extend the lifetime of the drops up to hours and days even in the absence of electrostatic, steric or other repulsion. In contrast, when the bulk phases are equilibrated with respect to the surfactant distribution but the adsorption has not reached yet its equilibrium value the emulsion stability can be very low even at high bulk surfactant concentrations.

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## 58.A4

### CONCENTRATED EMULSION STABILISED BY NON-IONIC SURFACTANTS

B. Deminière, T. Stora, A. Colin, J. Bibette

*C.R.P.P., C.N.R.S., Pessac, France*

We have studied the stability of monodisperse silicone in water emulsions (0.3 to 1.5 microns) stabilised by non-ionic surfactants. The rate of coalescence of these highly concentrated emulsions is followed by small angle light-scattering and by droplets size measurements. Above a critical temperature, coalescence is fast and leads to a new monodisperse emulsion with larger droplets (3 to 15 microns). The temperature threshold is independant on the oil fraction and on the size of the initial droplets. It is only related to the chemical nature of the surfactant. We show that this particular way of coalescence is related to

the phase diagram of the surfactant. The temperature threshold is equal to the temperature transition of the L1-L2 phase. It is suggested that the L2 phase plays the role of antifoam by emerging into both silicone-water surfaces of emulsion film and by dewetting.

Upon heating, the emulsion continues to coalesce slowly, keeping a narrow distribution. This allows us to prepare monodisperse emulsion with characteristic size as large as 40 microns.

## 59.A4

### COALESCENCE IN EMULSIONS

**B. Deminière, A. Colin, F. Leal Calderon, J. Bibette**

*Centre de Recherche Paul Pascal, C. N. R. S., 33600 Pessac, France*

We study the coalescence of concentrated and monodisperse oil in water emulsions, stabilized by non-ionic surfactants such as  $C_{12}E_5$  or  $NP_6$ .

Above a critical temperature, coalescence proceeds in two steps: in the first step, coalescence occurs very fast and leads to a new highly monodisperse emulsion with larger droplets. During the second step, the emulsion coalesces slowly, still keeping a quite narrow size distribution. The temperature threshold above which we observe this scenario is equal to the nucleation temperature of  $L_2$  phase (inverse micellar phase) in the continuous  $L_1$  phase (direct micellar phase). The first stage of coalescence is consistent with a dewetting mechanism where the  $L_2$  phase plays the role of an antifoaming agent.

In the second stage, the characteristic size  $R$  of the droplets scales as  $(\omega t)^{-1/2}$  where  $\omega$  is the frequency of coalescence per unit surface and  $t$  the time. This coalescence process is thermally activated and controlled by an energy barrier  $E_a$  such as  $\omega = \omega_0 \exp(-E_a/kT)$ . We study the influence of the different experimental parameters affecting  $E_a$ : the surface tension, the initial size of droplets, the oil volume fraction and the temperature.

## 60.A4

### FORMATION OF A STABLE HIGHLY CONCENTRATED O/W EMULSION, MODELLED BY MEANS OF FOAM FILMS

**R. Ivanova<sup>1</sup>, B. Balinov<sup>2</sup>, D. Exerowa<sup>1</sup>**

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*

<sup>2</sup>*Nycomed Imaging AS, Oslo, Norway*

Emulsions with a high volume fraction of the dispersed phase (up to 99%) are both of fundamental and industrial interest. The long-term stability of such emulsions is crucial for their formation and practical applications. It is well-known that block copolymers are good steric stabilizers. They can stabilize a large variety of colloid dispersions by preventing the droplet coalescence, with the adsorbed polymer layers interacting. The well-recognised foam-like structure of the highly concentrated emulsions is used to relate the properties of the foam films to the corresponding thin films in the emulsions. We have studied model microscopic foam films to gain deeper understanding of the stabilization mechanism in foams and highly concentrated emulsions. A PEO-PPO-PEO block copolymer (Synperonic FI08) is used to stabilize both the foam films and the emulsion. The parameter equilibrium thickness of the foam films is investigated by means of the microinterferometric method. It has been shown that electrolyte concentration of  $3 \times 10^{-3}$  M is enough to suppress the electrostatic interactions. The steric stabilization dominates under these conditions, giving the equilibrium thickness of 50 nm at polymer concentrations within the range  $10^{-5}$ - $5 \times 10^{-4}$  M. The dependence of the surface force on film thickness (disjoining pressure isotherm) is directly measured by the thin liquid film - pressure balance method. The copolymer concentration is kept constant ( $C_s = 4 \times 10^{-4}$  M), while the electrolyte concentration varies in a wide range ( $C_e = 0$ -0.05 M NaCl). It is illustrated that the influence of the electrolyte is much more pronounced at low pressures, whereas at the highest applied pressure ( $P = 4 \times 10^4$  N/m<sup>2</sup>) the film thickness is between 23 nm and 21 nm. Thus, copolymer concentration of  $4 \times 10^{-4}$  M is chosen to stabilize the highly concentrated O/W emulsion containing 86 wt% heptane as a dispersed phase. The droplet size distribution and the emulsion stability are controlled by the NMR self diffusion method that confirms the formation of a stable highly concentrated emulsion under these

conditions. The study demonstrates the ability to model the stability of highly concentrated emulsions by studying the interactions between the adsorbed polymer layers, measuring the disjoining pressure isotherms in single foam films.

## 61.A4 EMULSIFYING PROPERTIES OF ETHANOL-PRECIPITATED MUCILAGE FROM CELLULASE-HYDROLYSATE OF A GREEN ALGAE *MONOSTROMA NITIDUM*

Jenn-Shou Tsai, Tzong-Fuu Chiou, Jan-Jeng Huang and Bonnie Sun Pan

Dept. of Marine Food Science, National Taiwan Ocean Univ., Keelung, Taiwan, Republic of China

The emulsifying properties of ethanol-precipitated mucilage from cellulase hydrolasate of *Monostroma nitidum* were investigated. Both emulsifying activity and emulsion stability of mucilage increased from 51.5 and 48.0% to 69.0 and 62.0%, respectively, and oil did not separate from the emulsion when the concentration was at 1%(w/v). Increased protein and carbohydrate content was found by gel permeation chromatography in the high molecular weight area of mucilage. Increasing the mucilage concentration of the solution (0-20 mg/ml) led to a reduction of surface tension to 54.9 dyne/cm, and the emulsifying activity and emulsion stability increased to 76.9 and 70.0%, respectively. The oil did not separate from the emulsion when the solution concentration was higher than 0.5%(w/v). When 0.2% NaCl was added to the mucilage solution, apparent viscosity decreased from 37.1 to 7.6 cps; the emulsifying activity and emulsion stability decreased from 69.0 and 62.0% to 50.0 and 48.0%, respectively.

## 62.A4 EFFECT OF THE INTERFACIAL BENDING MOMENT ON THE FLOCCULATION IN EMULSIONS

P. A. Kralchevsky and T. D. Gurkov

Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics Faculty of Chemistry, University of Sofia, 1 James Bourchier Avenue, Sofia 1126, Bulgaria

The work of *dilatational* deformation of an interface is determined by the surface tension,  $\sigma$ , and the surface (Gibbs) elasticity; likewise, the work of *flexural* deformation of an interface is determined by the interfacial bending moment,  $B_0$ , and the curvature elastic moduli,  $k_c$  and  $\bar{k}_c$ . In fact, the bending moment is related ( $B_0 = 2\sigma\delta$ ) to the *Tolman length*,  $\delta$ , which determines the curvature dependence of surface tension. On the other hand,  $B_0$  is related ( $B_0 = -4k_c H_0$ ) to the spontaneous curvature,  $H_0$ , which was initially introduced in the theory of lipid membranes.

Similarly to the disjoining pressure in the liquid films the interfacial bending moment,  $B_0$ , (as well as  $k_c$  and  $\bar{k}_c$ ) can be expressed as a superposition of contributions due to the various surface forces: electrostatic, van der Waals, steric, etc. We derived theoretical expressions for the electrostatic and van der Waals contributions in  $B_0$ . In particular, it turns out that the electrostatic component of  $B_0$  is proportional to the square of the surface Volta potential,  $\Delta V$ , and can be determined by surface potential measurements [1]. In the case of liquid-gas interfaces the electrostatic and van der Waals contributions in  $B_0$  have the opposite signs. In contrast, for oil-water interfaces these two components of  $B_0$  have the same sign and tend to bend around the oil phase. The droplets in emulsions are deformable and deform upon collision. For O/W emulsions  $B_0$  usually opposes the flattening of the droplet surfaces in the zone of collision but for W/O emulsions  $B_0$  favors the flattening [2]. Consequently, the interfacial bending moment stabilizes the O/W emulsions, but destabilizes the W/O ones. It turns out that this effect of the bending moment can be important even for droplets of  $\mu\text{m}$  size [2].

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## 63.A4 STRUCTURE ELUCIDATION OF LATEXES CONTAINING WATER BY <sup>1</sup>H-SPIN DIFFUSION NMR-EXPERIMENTS

F. Mellinger<sup>1</sup>, M. Wilhelm<sup>1</sup>, K. Landfester<sup>1</sup>, H. W. Spiess<sup>1</sup>, A. Haunschild<sup>2</sup>

<sup>1</sup>Max-Planck-Institute for Polymer Research, 55128 Mainz, Germany

<sup>2</sup>BASF AG, 67056 Ludwigshafen, Germany

Solid state NMR is a powerful tool to elucidate structure, dynamic and orientation<sup>1,2</sup> in polymers. <sup>1</sup>H-spin diffusion provides structural information about heterogeneous polymers. Spin diffusion experiments combine the information of <sup>1</sup>H-spectra with respect to mobilities with spatial information by analyzing the time dependent <sup>1</sup>H-spin magnetization behaviour<sup>3</sup>. This method is used to determine the domain sizes of copolymers and blends but also to investigate more complex structures like interfaces in core-shell latices. Especially hard/soft systems with phases containing mobile and rigid protons are particularly well suited for spin diffusion experiments.

We use spin-diffusion experiments to elucidate global structures in complex heterogeneous polymer latexes. We observe a complex remagnetisation effects during spin-diffusion experiments in a three component system with one rigid and two different soft phases. As these effects can only occur when the two magnetisation source regions are spatially separated, it facilitates the interpretation of spin diffusion data for structure investigation of latex structures.

The investigated system consists of a heterogeneous PBuA/PS/PAA latex synthesized in a two step emulsion polymerisation. The final film still contains water. Films were dried to prevent interdiffusion and to retain the original latex structure. We demonstrate that the latex possesses an inverse structure, where the second step copolymers polymerizes inside the seed particle. Additionally, the measured data indicates the presence of a mixing gradient inside the latex particle, where the core itself contains seed polymer. Through the help of a scaling law for the spin diffusion constants of the mobile phases, the approximate domain size of the mobile heterogeneities inside the core are measured to be ca. 4 nm<sup>4</sup>.

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## 64.A4 WAX AND STABILITY OF CRUDE OIL EMULSIONS

Mingyuan Li

*School of Petrochemical Engineering, University of Petroleum, Changping, Beijing 102200, China*

Based on study of the influence of wax fraction from North Sea and Daqing crude oils on the stability of a model emulsion, it was found that the wax fractions from the crude oils were not only contain non polar components, like paraffin wax, but also contain some polar components, such as fatty acid, fatty alcohol and fatty amine. Therefore, the wax fractions have interfacially active characteristics. Compare with the resin and asphaltene fractions from the crude oils, the wax fractions have higher polarity. When low melting point wax fractions were dissolved in oil phase, the fractions were able to substituted the resin and asphaltene fractions from the interface between water and oil. Therefore, decrease the interfacial tension of the system and the stability of the emulsions. When temperature was low, the wax fractions of higher melting point were crystallized. Due to the wax crystals contain some polar components, the wax crystals were wetted by both water and oil phases, and absorbed in the interface of water and oil. The wax crystals



were serving as a mechanical barrier to prevent the coalescence of the water droplets and enhanced the stability of the emulsions.

## 65.A4

### HOMOGENEOUS NUCLEATION IN A MONODISPERSE OIL-IN-WATER EMULSION

Jane Morris, Ulf Olsson, Håkan Wennerström

*Physical Chemistry 1, Chemical Centre, Lund University, Lund, Sweden.*

The work presented here is concerned with the mechanism of the separation of the oil phase from an oil-in-water microemulsion, stabilized by nonionic surfactant, as the temperature is decreased from the one phase region across the solubilisation limiting phase boundary (SPB). At equilibrium after the temperature quench a droplet emulsion phase coexists with excess oil. The first stage of the equilibration process with decreasing temperature is followed by measurement of turbidity. It is observed that for small temperature quenches the system is metastable. However a sharp boundary is observed as the temperature is decreased further, beyond which the system is unstable and oil phase separation occurs instantaneously. The existence of a metastable/unstable phase boundary is reproducible for different droplet concentrations, for varying initial droplet sizes, and for different oils. A homogenous nucleation process is proposed where one oil drop grows allowing others to decrease monotonically in size. The driving force for phase separation and the presence of the nucleation threshold is described in terms of the curvature free energy of the surfactant film.

## 66.A4

### STABILITY OF SPRAY-DRIED EMULSIONS

M. Morvan and G. Guérin

*Rhône Poulenc, Centre de Recherches d'Aubervilliers 52, Rue de la Haie Coq,  
93308 Aubervilliers Cedex -France*

Spray-drying of dispersions is a common way of preparing concentrated products easy to handle and easy to mix with other ingredients. This technique is widely used to produce powders made from latex or agrochemical active ingredients. However there exist in the literature few examples of spray-dried oil-in-water emulsions, with an oil volume fraction exceeding 0,7. In this paper we described such a system based on a vaseline oil emulsion stabilized with a sugar type surfactant. Narrow size distribution emulsions were prepared using a high pressure apparatus. They were composed of 36 % (weight) of vaseline oil, 4 % of surfactant and 60 % of distilled water. In order to understand the stability of the dried emulsion, the effect of the sugar surfactant was compared to that of a sodium dodecyl sulfate (SDS). The emulsion stability was studied using the osmotic stress technique. After one month equilibration in the reservoir, the SDS stabilized emulsion undergoes coalescence at oil volume fraction above 0,6 while the sugar surfactant emulsion remains stable (same size distribution). In that case a cryoTEM image clearly shows individual deformed particles. On a semilog scale, osmotic pressure increases almost linearly as a function of the oil volume fraction  $\Phi$ . However at  $\Phi = 0,74$  which corresponds to the closest packing of spheres, the slope changes abruptly to become less steep. The binary phase diagram of the sugar type surfactant in water was determined using Small Angle X-ray Scattering experiments. A temperature independent hexagonal liquid crystalline phase occurs for a surfactant concentration in water above 60 % w/w. This phase is in equilibrium with a solid crystal for surfactant concentration above 85 %w/w. If we consider a fcc structure in the concentrated emulsion, then rhombic dodecahedron cells<sup>3</sup> are obtained when the soft spheres are packed. Taking into account this structural model, both the distances between droplet interfaces and the oil volume fraction were estimated for various composition in the binary phase diagram. The occurrence of the liquid crystalline hexagonal phase appears for oil volume fraction equal to 0,88, the thickness between droplets being equal to 20 nm. These results suggest that the stability of spray-dried emulsions is related to a matrix effect where a temperature independent "rigid" phase is formed during compression.

## 67.A4 MOLECULAR MOBILITY IN SYSTEM OF RL/PAA-WATER-OIL. EMULSIONS FOR PHARMACY

V.V. Rodin<sup>1</sup>, V.N. Izmailova<sup>2</sup>, V.I. Gaitan<sup>3</sup>, K.V. Alekseev<sup>4</sup>

<sup>1</sup>*Institute of Physical Chemistry (RAS), Moscow, Russia*

<sup>2</sup>*Moscow State University, Moscow*

<sup>3</sup>*State Research Centre for Applied Microbiology, Moscow region;*

<sup>4</sup>*SIA "Biotechnologia", Moscow*

Rarely-linked polyacrylic acid (RL/PAA) is used as macromolecular carrier of drug in some medical forms: gels, suspensions, emulsions. Water/oil emulsions can be obtained by sonication of RL/PAA-water system in the presence of medical light oil. Water diffusion and molecular mobility in these emulsions are very essential because the ones are responsible for drug release and long action of preparation. NMR-methods can be used for studies of such systems [1-4]. The work examines the RL/PAA-water-oil system at formation of emulsions in the presence of some additives: propyleneglycol (PG), ethanol three-ethanolamine (TEA), surfactant (twin). NMR-relaxation and pulsed gradient spin echo methods were used to receive an additional information concerning the mechanism of increase of drug effect. Three components of spin-spin relaxation time ( $T_2$ ) were observed for RL/PAA-water gels. Diffusion coefficient ( $D$ ) for motial protons was about  $0.8 \cdot 10^{-5} \text{ cm}^2/\text{s}$  (for bulk water the one was  $2.3 \cdot 10^{-5} \text{ cm}^2/\text{s}$  [1,4]. The presence of TEA diminishes the fast component of  $T_2$  (to 43 ms) and increases the fraction of free water. The diminishing of  $D$ -value (to  $0.40 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ) testifies the decrease of translational mobility of molecules. The  $T_1$  and  $T_2$ -values of long component in emulsions (RL/PAA-water-oil) were the same as the ones without oil. Long  $T_2$  component in emulsions was associated with water protons and exchange protons of polymer but fast one was responsible for the oil protons. Minimum in  $T_1$ -data was observed at 5% of oil.  $T_2$ -dependence on oil concentration confirmed this minimum too. For dividing of rotational and translational parts in  $T_1$  the diffusion coefficient in emulsions was measured at 5% of oil ( $D \approx 1.9 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ). The most change of molecular mobility was responsible for decrease of rotation of molecules [4]. When 5% of oil was added to RL/PAA-water in the presence of twin-80 the  $T_2$ -value of water component in emulsions was decreased. In the presence of the same surfactant the diffusion coefficient in emulsions with 5% of oil was decreased to  $1.6 \cdot 10^{-5} \text{ cm}^2/\text{s}$ . (twin-80 in water results in  $D = 2.0 \cdot 10^{-5} \text{ cm}^2/\text{s}$ ). The data obtained: show possibilities of NMR-approaches for study of molecular dynamics of polymer gels and water properties in emulsions in the presence of additives. Two tendencies were observed for PG and TEA. A possibility of formation of complexes of PG and ethanol molecules was observed. The participation of polymer chains in stabilization of water/oil emulsions may be tested with dividing of rotational and translational mobility of molecules.

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## 68.A4 EMULSIONS AND MICROEMULSIONS. A COMPARISON

Eli Ruckenstein

*Department of Chemical Engineering State University of New York at Buffalo Buffalo,  
New York 14260 USA*

Emulsions and microemulsions are very different kinds of dispersions, since the former have only kinetic stability, while the latter are thermodynamically stable. They have, however, something in common and Shinoda noted a parallelism between the two regarding the phase inversion when the temperature is changed. The goal is to explain the parallelism, to examine the stability of emulsions with regard to temperature and to show that a two-scale thermodynamics can explain the most relevant experimental observations regarding microemulsions.

## 69.A4 MICROEMULSION FORMATION AND ITS ROLE IN THE PROCESS OF SYNTHESIS OF ULTRA-DISPERSED MINERAL FILLER PARTICLES IN POLYMER MATRIX

G.A. Simakova, I.A. Tutorsky

*Moscow Academy of Fine Chemical Technology named after M.V.Lomonosov, Moscow, Russian Federation*

A new method, based on the theory of ultra-dispersion state, is suggested for structural modification of elastomeres by ultra-dispersed particles of fillers, synthesized in rubber solutions or in latex. Insoluble solid-phase particles of alkaline-earth metals sulphates, carbonates and phosphates were obtained by neutralization reaction or by ion-exchange reaction carried out *in situ* in rubber solution. The reaction of salt particles synthesis is held in Water - SAS - Rubber solution system, which is the reverse emulsion whose parameters, such as dispersion grade and stability, were the major factors to determine the size of filler particles and uniformity of their distribution in polymer matrix. The following conditions are required for obtaining of microemulsion of Water/Oil type: 1) low values of inter-phase tension on the water-hydrocarbon phase boarder; 2) SAS (surface active substance) used in the process must have the value of distribution coefficient which will provide for the diffusion float of SAS through the phase boarder and for the microemulsion formation; 3) high surface activity of SAS is required to achieve in non-equilibrium conditions the concentration higher than in the state of equilibrium. Increase in electrolytic concentration as well as increase of SAS hydrocarbon chain length will lead to the formation of microemulsion of Water/Oil type.

## 70.A4 HYDRODYNAMIC INTERACTIONS BETWEEN FLUID PARTICLES IN THE EMULSIONS

Simeon D. Stoyanov and Ivan B. Ivanov

*Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

Typical emulsion system consists of small drops of one liquid immersed into the second one, thus hydrodynamic interaction of emulsion droplets at small separations is one of the major factors which determine the properties and stability in the emulsions.

We studied the relative motion of two spherical drops under Stokes flow conditions using bispherical coordinates. The influence of a surfactant which was soluble in both phases was taken into account. As the drops move together, the tangential balance of the stress on the drop interfaces is influenced by: presence of two fluids and the surfactant distribution in both phases. This surface force causes a tangential motion of the drop surfaces and drives a flow in the drops. That in turn has significant effect on the magnitude of the force resisting the approach of the drops.

The resulting series solution for the relative motion of two drops along their line of centres shows, that the hydrodynamic force opposing this motion increases without bound when the distance between the drops decreases, and even small amount of surfactant changes it significantly. When there is small amount of the surfactant which soluble only in the continuos phase, it "freezes", the drop surfaces and they behave as a solid ones. When there is a surfactant which soluble only in the dispersion phase, it increases the drag force, but the drop surfaces are tangentially mobile i.e. the increase of the drag force is much smaller compared to the previous case. The case when there is a surfactant which was soluble in both phases was also studied.

## 71.A4 THE BEHAVIOUR OF MODIFIED MONOACYLGLYCEROL EMULSIFIERS IN EMULSION SYSTEMS

Halina Szlag and Włodzimierz Zwierzykowski

*Department of the Technology of Fat and Detergents Technical University of Gdansk, Gdansk, Poland*

Modified acylglycerol emulsifiers with programmed values of hydrophile - lipophile balance were synthesized *in situ* by esterification of glycerol with fatty acids in the presence of fatty acid soaps.

The modification of the surface activity of the emulsifier was obtained by programming sodium or potassium soap content and hydrocarbon chain length, as well as the length of the fatty acid acyls in the monoacyl glycerol.

These products show an interaction of nonionic - monoacyl glycerols and anionic - fatty acid salts, and may be used for the preparation of O/W emulsions.

The effectiveness of the synthesized emulsifiers was investigated in model emulsion systems.

The influence of the phase volume ratio on emulsion inversion, stability and emulsion droplet size was studied. The linear correlation between the HLB value of emulsifiers used and conductivity of the obtained O/W emulsions were observed.

It was stated, that for given emulsion systems hydrophobic properties of oil phase and volume ratio influence the required HLB value of the emulsifier, which should be used.

## 72.A4 THERMAL PROPERTIES OF HEXADECANE EMULSION STABILIZED WITH DIMYRISTOYLPHOSPHATIDYLCHOLINE

Kazuo Tajima<sup>1</sup>, Yoko Imai<sup>1</sup>, Akio Nakamura<sup>2</sup>, and Masakatsu Koshinuma<sup>3</sup>

<sup>1</sup>*Department of Chemistry, Faculty of Engineering, Kanagawa University,  
3-27 Rokkakubashi, Yokohama, 221*

<sup>2</sup>*Laboratory of Chemistry, School of Design and Architecture, Nagoya City University,  
2-1 Kitachikusa, Chikusa-ku, Nagaya 464*

<sup>3</sup>*Laboratory of Chemistry, Faculty of Informatics, Teikyo Heisei University, 2289-23 Uruido,  
Ichihara, Chiba 290-01*

Emulsification of hexadecane with dimyristoylphosphatidylcholine (DMPC) in the ( $L_{\alpha}$ +H<sub>2</sub>O) phase has been investigated as a function of temperature<sup>1</sup>. Average particle size of the emulsion prepared under the constant conditions was about 800 nm up to the higher-order transition temperature,  $T^*$  (29.0°C), which was a few degrees higher than the gel-liquid crystal transition temperature,  $T_m$  (23.7°C)<sup>2</sup>. Above  $T^*$ , however, the sizes of the emulsion sharply decreased and reached about 390 nm. The temperature dependence of hexadecane concentrations caused by creaming was explained with the emulsion particle size. Zeta-potential of the emulsion surface was also shifted to -15 mV, at  $T^*$  from -36 mV. Interfacial tension at hexadecane-DMPC dispersion interface decreased with increasing temperature until  $T^*$ , and then reached almost a constant value less than 1 mN m<sup>-1</sup>.

These novel phenomena were understood by the idea that thermal character of DMPC dispersion used as an emulsifier changed definitely at  $T^*$  besides  $T_m$ . Furthermore, it was estimated from the relation between the amount of DMPC and the total surface area calculated from the particle size of emulsion, that the surface of hexadecane emulsion was covered with triple layers of DMPC below  $T^*$ , and with monolayer above  $T^*$ . Consequently, it was concluded that the thermal properties of hexadecane emulsion was strongly depended on the thermal state of DMPC lamellar liquid crystal used as an emulsifier.

1 K. Tajima, Y. Imai, A. Nakamura, M. Koshinuma, *J. Jpn. Oil. Chem. Soc.*, 46, No.3, (1997).

2 K. Tajima, Y. Imai, T. Horiuchi, M. Koshinuma, A. Nakamura, *Lanmuir*, in press.

**73.A4****PREPARATION AND STABILITY OF O/W EMULSIONS OF  
OLEOPHILIC TETRAHYDROXYETHYLATED ISONONYLPHENOL****H.M. Zadymova, Z.N. Markina***Department of Chemistry, Moscow Lomonosov State University, Moscow, Russia*

The immobilization of oleophilic liquid tetrahydroxyethylated isononylphenol (Neonol NE<sub>4</sub>) in water and aqueous solutions of electrolytes (Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>) by ultrasonic dispersion in the presence of water-soluble nonionic surfactants [dodecahydroxyethylated isononylphenol (Neonol NE<sub>12</sub>) and ethylene oxide-propylene oxide block copolymer (Proxanol 268) was studied. Using a modification of the flow-through ultramicroscope with a laser light source, polarization analyzer, and automated counting of the number of particles, dispersion analysis of the prepared oil-in-water emulsions was performed as a function of their "age" ( $\tau$ ) at 293 K. It was found that the dependence on  $\tau$  of dispersity of investigated emulsions has maximum. For Proxanol 268 and Neonol NE<sub>12</sub> as emulsifiers, the effect of spontaneous dispersion was discovered in less than 4 and 9 days, respectively. A mechanism accounting for the spontaneous dispersion of these emulsions was suggested. The conditions enabling the preparation of stable fine emulsions ( $r \approx 65$  nm) of Neonol NE<sub>4</sub>), which may be used as effective technical detergents, were identified.

**74.A5****STRUCTURE OF SOLUTION OF ULTRADISPERSION DIAMONDS****L.V. Agibalova, V.Ju. Dolmatov, V.V. Klyubin, A.P. Voznjakovsky***Lebedev Research Institute of Synthetic Rubber, St. Petersburg, Russia*

At the moment in the colloidal science there is significant interest to properties of ultradispersion solid substances. Ultradispersive systems have considerable excess Gibbs energy caused by the contribution of surface energy. The large interface in these systems is the reason for their instability in solutions. The trend to reduce a value of free energy causes reduction of degree of dispersion in these systems and leads to coagulation.

In this investigation the structure of ultradispersion diamonds (UDD) in various liquids was studied. For the research synthetic UDD were used obtained by detonated decomposition and further condensation of products of explosion under a lack of oxygen. The dispersion structure of formed thus UDD-powders is not investigated sufficiently at present.

Electron microscopic and x-ray measurements have shown that during condensation there arise microparticles with crystal structure of diamond and sizes of about 4-6 nm. During further condensation and storage these microscopic crystals of diamond incorporate in secondary units. At the moment researches carried out with the help of various methods did not yield a satisfactory answer on the question: what is the dispersive structure of these secondary units.

In this study we have investigated dispersive structure of secondary units of UDD in liquids and their stability. The researches of dispersive structure were carried out with the help of the dynamic light scattering method. UDD-powders were dispersed in water and some organic solvents. All the samples before measurements were irradiated by ultrasonic. Time of exposition power were varied within wide limits.

In result of numerous experiments it was established that the secondary units have wide distribution, extending from 0.2 microns up to 20 microns. The units of the large sizes are not stable and they can be demolished on steady units with the size of about 0.2 micron. These units are rather steady in relation to ultrasonic influence and they are not broken under increase of ultrasonic power and change of the environment properties. We consider that these dispersive structures are alloyed units of microcrystals of diamond formed during high-temperature condensation. The units of the large sizes are easily destroyed on action of ultrasonic, especially, in polar liquids.

## 75.A5

POLYEMPIRICAL METHOD OF DETERMINATION OF  
DISTRIBUTION FUNCTION OF  $\text{Fe}_3\text{O}_4$  NANOPARTICLES ON SIZE

Rasim A. Ali-Zade

*Institute of Physics, Azerbaijan Academy of Sciences, Azerbaijan, Baku 370143, H. Javid st. 33*

True histogramme of distribution of system of  $\text{Fe}_3\text{O}_4$  nanoparticules on size has been obtained on the base calculation agreement between firing ground frequency and histogramme distribution obtaining in different values of division of interval changing size of particles, which are determined from electron microphotography of samples. Investigation of agreement of histogrammes and firing ground frequency has been carry out with  $\chi^2$  criterion and nearity two function methods and has been obtained following values of division 5, 5, 6, 5 for system of  $\text{Fe}_3\text{O}_4$  nanoparticles with average size 9.5, 7.7, 7.3, 5.4 nm correspondingly for MF-I, MF-II, MF-III, MMS ( $\text{Fe}_3\text{O}_4$ ) (MF -magnetic fluid, MMS ( $\text{Fe}_3\text{O}_4$ ) - polymeric microspheres filled with  $\text{Fe}_3\text{O}_4$  nanoparticles). First four initial moments of distribution, coefficients asymmetry and polydispersity calculating with firing ground frequency and true histogramme for MF-II are 7.7 nm, 65.5 nm<sup>2</sup>, 600.5 nm<sup>3</sup>, 5951.7 nm<sup>4</sup>, 0.82, 1.366 and 7.6 nm, 62.8 nm<sup>2</sup>, 567.1 nm<sup>3</sup>, 5520.3 nm<sup>4</sup>, 0.76, 1.257.

Distribution function has been determined on the base investigation agreement true histogramme with normal, log-normal and  $\chi^2$  function with  $\chi^2$  criterion, nearity of two function and diagramme quantilies methods. Investigation showed, that distribution function of  $\text{Fe}_3\text{O}_4$  nanoparticles on size is good described with log-normal function. Results of investigation agreement with diagramme quantilies method for MF-III are 0.95, 0.98, 0.97, 0.74. As see value of investigation with diagramme quantilies method for log-normal function is 0.98 and large another. Average size of systems determining with log-normal function are 9.5, 7.5, 7.3, 5.4 nm. Magnetisation curves obtaining with log-normal function, true histogramme and experimental are good agree.

## 76.A5

IRON OXIDE NANOPARTICLES AS MRI CONTRAST AGENTS:  
INFLUENCING PARAMETERS ON SYNTHESIS

Babes L., Denizot B., Tanguy G., Le Jeune J.J., Jallet P.

*Laboratoire de Biophysique, Faculté de Médecine, 49045 Angers, France*

Contrast agents, which enhance contrasts by modifying tissues relaxation times, are nowadays widely used in magnetic resonance imaging MRI. Superparamagnetic particles actually used are constituted by a small iron oxide core (diameter 5 to 15 nm), coated generally by a thick polysac-charidic layer (total diameter 30 to 100 nm) and formulated by direct coprecipitation of iron compounds in presence of polymeric material. Our goal was to formulate easily new stable uncoated superparamagnetic particles of small sizes.

Colloids were generated by coprecipitation of an aqueous solution of iron salts and tetramethyl-ammonium hydroxyde solution, in which stable suspensions are obtained. The iron mixture ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) was injected through a catheter ( $\varnothing_{\text{int}} = 0.38$  mm) in the circulating flux ( $\varnothing_{\text{int}} = 8$  mm) of the TMAOH (1M) solution. Flux rates of Fe and TMA solutions were controled by peristaltic pumps. After magnetic deposition on magnets, the basic colloidal solution obtained was electromagnetically filtered. Influences of parameters such as media composition (comparison between a TMA and a mixture of TMA and ammonia  $\text{NH}_3$  media),  $\text{FeCl}_2$ - $\text{FeCl}_3$  media ( $0/10 \leq \text{Fe}^{2+}/\text{Fe}^{3+} \leq 8/10$  M/M), injection fluxes ( $1 \leq \text{Fe flow} \leq 5$  ml/min and  $50 \leq \text{TMA flux} \leq 800$  ml/min), concentrations ( $12.93 \leq [\text{Fe}] \leq 116.4$  mM and  $0.25 \leq [\text{TMA}] \leq 2$  M), temperature ( $20^\circ\text{C} \leq T \leq 80^\circ\text{C}$ ) and influence of oxygen (solutions partly degased) on transmission electron microscopic size, magnetic and MR relaxometric properties and colloidal stability of particles, were evaluated.

We have determined the relative importance of these parameters, as well as the optimal conditions for obtaining uncoated stable particles, with an average size of 5 nm and interesting relaxivities. Among these, only TMA concentration and temperature do not greatly influence the synthesis results. The optimal values were: iron concentration 38,6 mM,  $\text{Fe}^{2+}/\text{Fe}^{3+} \approx 0,5$ , Fe flow  $\approx 2$  ml/min, TMA flux 500 ml/min. In these conditions, nanoparticle suspensions fulfill at appropriate MR conditions.

The interpretation of the observed limits takes into account diffusibilities of reactants and products, feeding rates of reactants and surface properties of nanoparticles. A model of the synthesis, related to the spontaneous emulsification of suspensions, is proposed.

## 77.A5 KINETICS OF NANOPARTICLE ADSORPTION STUDIED BY OPTICAL REFLECTOMETRY

M.R. Böhmer and L.G.J. Fokkink

*Philips Research P.O.80.000, 5600 JA Eindhoven, The Netherlands*

The kinetics of adsorption of nano-sized  $\text{SiO}_2$  particles were followed in situ by using optical reflectometry in stagnation point flow. The initial adsorption rate decreases with increasing particle size. The effects of salt concentration on the plateau adsorbed amounts can be accounted for by an effective hard sphere concept. A diffusion enhanced random sequential adsorption mechanism describes the observed kinetics. Cationic poly-electrolytes are very efficient to induce silica adhesion and competition effects between  $\text{SiO}_2$  particles and polymers in solution are shown. Repeated sequential adsorption of polymer and particles can lead to controllable high amounts of particles on the surface. Strategies to obtain well defined, predetermined degrees of surface coverage are discussed.

## 78.A5 SYNTHESIS AND STABILIZATION OF SILICA-COATED CdS SEMICONDUCTOR NANOPARTICLES

Miguel A. Correa-Duarte, Luis M. Liz-Marzán

*Departamento de Química Física e Química Orgánica, Universidade de Vigo, Apdo. 874, 36200 Vigo, Spain*

CdS semiconductor particles in the nanometer size range were synthesized by coprecipitation of  $\text{Cd}^{2+}$  and  $\text{S}^{2-}$  ions in the presence of citrate, which acted as a stabilizer. The stability of such nanoparticles against flocculation is limited with respect to the ionic strength of the dispersion. Furthermore, the citrate-coated particles are easily degraded through photochemical oxidation in the presence of dissolved oxygen.

These two processes are slowed down, or even completely avoided, when a homogeneous silica shell is built up around the particles. The damping of the oxidation arises from the limited access of  $\text{O}_2$  molecules to the CdS surface, when this is surrounded by microporous silica.

The coating procedure consists of three main steps, mainly: a first step where citrate ions are exchanged for 3-(mercaptopropyl) trimethoxy silane (TPM); then the deposition of a thin silica shell through addition of a sodium silicate solution at a pH low enough for silica precipitation; and finally transfer of the dispersion into ethanol, where thicker shells can be grown via Stöber synthesis.

The growth of thick shells on individual CdS cores can finally lead to the preparation of concentrated dispersions with an intercore spacing tailored through the thickness of the shell. Such dispersions are suitable for the ultimate preparation of materials with non-linear optical properties.

## 79.A5 GROWING OF NANOPARTICLES AT S/L ADSORPTION LAYER IN BINARY LIQUIDS

Imre Dékány<sup>1</sup>, László Turi<sup>1</sup>, Anna Szücs<sup>1</sup>, Ferenc Berger<sup>1</sup>, Zoltán Király<sup>1</sup>, János H. Fendler<sup>2</sup>

<sup>1</sup>*Department of Colloid Chemistry Attila József University, H-6720 Szeged, Hungary*

<sup>2</sup>*Syracuse University Department of Chemistry, Syracuse, N.Y.13244-4100 USA*

The solid/liquid interfacial adsorption layer is eminently suitable for the preparation of size quantized nanoparticles if it can be assured that the particles be generated exclusively in the interfacial layer, functioning as a nanophase reactor. In binary mixtures (methanol-toluene and ethanol-cyclohexane)

the volume of the nanophase reactor, i.e. the thickness of the adsorption layer can be arbitrarily regulated depending upon the binary liquid composition and the hydrophilic/hydrophobic character of the support surface. This possibility is utilized for the preparation of semiconductor (CdS, ZnS, TiO<sub>2</sub>, ZnO) nanoparticles of varying size on SiO<sub>2</sub> aerosil, clay minerals, pillared clays and layer double hydroxides. Reduction of precursor ions is conducted exclusively in the nanophase reactor in alcoholic medium, while no particles may be formed in the toluene or cyclohexane rich liquid bulk phase. The formation and the band gap energy of semiconductor nanoparticles was monitored by UV-VIS spectroscopy. The Pd and Pt metal content on the solid support was determined by adsorption measurement.

The interlamellar distance of swelling layer silicates depends upon composition. In this case, nanoparticles are formed within the interlamellar space and size quantization may be altered by modifying the composition of polarity of the binary mixtures.

The size of nanoparticles on supports is determined by TEM and SAXS measurements. Their catalytic properties are characterized by microcalorimetric monitoring of hydrogen uptake and by liquid phase hydrogenating reactions in stirring vibration reactor.

The rheological characteristic of the suspension containing nanoparticles are basically different from those of the original suspension, therefore the analysis of flow curves also allowed conclusions to be drawn regarding the formation of nanoparticle bridges and their structure building properties. It was established that particle size depended upon the quality and composition of the binary mixtures used and the surfacial concentration of precursors on the support. The SAXS measuring technique was successfully applied to the determination of particle size and the characterization of the structure of the support.

## 80.A5 SPECTROPHOTOMETRIC STUDY OF COLLOIDAL GOLD CONDENSATION UNDER THE ACTION OF MACROMOLECULAR REDUCER

Dykman L.A., Bogatyrev V.A., and Shchyogolev S.Yu.

*Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences,  
Pr. Entuziastov 13, Saratov 410015, Russia*

Cytochemical methods based on the use of colloidal gold conjugates as biospecific markers are becoming more and more significant in modern medical and biological investigations. Reduction of hydrogen tetrachloroaurate (HAuCl<sub>4</sub>) by sodium citrate is a conventional way of production of gold soles. It is regarded to proceed according to the mechanism of chemical condensation (Zsigmondy's theory) including the steps of nucleation, reversible aggregation (peptization) and particle ageing. However, of interest are data on specific features and mechanisms of HAuCl<sub>4</sub> reduction by some other reducing agents (in particular, macromolecular species).

We performed a spectrophotometric study on the kinetics of formation of gold soles during reduction of HAuCl<sub>4</sub> by polyethylene imine. The data were compared with those obtained using the conventional sodium citrate procedure (see above). Attenuation spectra of the reaction mixture in the wavelength range of  $\lambda=300-750$  nm were measured after certain time intervals using a Specord M 40 spectrophotometer in a cuvette with controlled heating. Interpretation of the results was based on the fact that gold (III) halogenides have a typical absorption region of 320 to 340 nm, while the maximum of the characteristic attenuation for metallic gold particles is within the region of  $\lambda=500-550$  nm (depending on the sole particle size).

Significant differences in the reduction rate were registered: the latter was relatively high in the case of sodium citrate and essentially lower in the case of polyethylene imine. In both cases, an optical density decrease in the short wave spectral region was observed at the initial stages of the reactions, which can probably be due to a decrease in the concentration of ionic gold. At the same time, light attenuation in the spectral region of  $\lambda=500-550$  nm was insignificant in both cases. Further, however, the spectral characteristics of the objects under study became essentially different. In the case of sodium citrate a sharp increase of optical density in the long wave spectral region was observed followed by a gradual shift of the attenuation band maximum from 700 nm to 520 nm. In the case of polyethylene imine no additional attenuation band was observed; there was only a gradual increase in optical density for the attenuation band with the maximum at 520 nm.



The differences registered can be explained on the basis of Zsigmondy's theory (see above). This mechanism is obviously valid in the case of sodium citrate (and probably for some other low molecular reducing agents). This is confirmed by the appearance and transformation of the light attenuation band in the relatively long wave spectral region.

The activity of polyethylene imine as a reducing agent for  $\text{HAuCl}_4$  turned out to be markedly lower. In addition, this compound has cationic properties and a significantly high molecular mass and is capable of adsorption onto the surface of gold particles (which bear a relatively high negative charge) resulting in stabilization of gold soles. All this could limit the critical size of the new phase nuclei at the level comparable by the order of magnitude to the final size of colloidal gold particles, reduce the particle growth rate and prevent peptization. This is evidenced by the fact that the position of the attenuation band maximum for the forming suspension at  $\lambda=520$  nm was practically time independent. Measurements of the average particle size of colloidal gold performed by the spectrophotometric and electron microscopy methods showed its 1.5 to 2-fold increase in the case of polyethylene imine.

Accordingly, the data obtained show that choosing an adequate reducing agent and taking into account the kinetic features of the colloid phase formation, it might principally be possible to obtain biospecific markers with a certain specified size of colloidal gold particles. This possibility seems to be of great importance with respect to the wide diameter range of gold labels which are used in preparing biomarkers, *viz.*, from 1-5 nm (electron microscopy) to 30-50 nm (light microscopy and solid phase immunoassay).

## 81.A5

### METAL SURFACTANTS AND NANOPARTICLES

Julian Eastoc and Barnaby Warne

*School of Chemistry, University of Bristol, Bristol, England.*

Nanoparticles have been produced by chemical reduction of specially prepared metal surfactants. Using water-in-oil microemulsions and lyotropic liquid crystal structures of these surfactants as templates. UV/Visible spectroscopy, SAXS, SANS and TEM micrographs show that the size of cobalt, nickel, copper and neodymium nanoparticles can be controlled in these systems. Also micron-sized anisotropic particles have been seen to form, such as needles and fibres.

## 82.A5

### COLLOID CHEMICAL APPROACH TO ADVANCED MATERIALS SYNTHESIS

Janos H. Fendler

*Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100, USA*

Two different approaches of "wet" chemical constructions of nanostructured materials will be highlighted in the lecture. The first approach involves the generation of nanoparticles and nano-particulate films in situ under monolayers spread on aqueous solutions and their subsequent transfer to solid substrates. Transfer of stabilized colloidal nanoparticles from an aqueous dispersion to the solid state represents the second approach. This transfer is affected by (i) forming a monoparticulate Langmuir film from the dispersed colloids on an aqueous solution surface and the subsequent layer-by-layer transfer of the film to a substrate by the Langmuir-Blodgett technique, (ii) introduction of the dispersed colloids between the polar head-groups of Langmuir-Blodgett films, and (iii) sequential self assembly of polyelectrolyte - colloidal nanoparticle sandwich films.

### 83.A5 NANOPARTICLES OF TERNARY SEMICONDUCTORS IN COLLOIDS: LOW-TEMPERATURE FORMATION AND QUANTUM-SIZE EFFECTS

V.S. Gurin

*Physico-Chemical Research Institute, Belarusian State University, Minsk, 220080, Belarus,*

The interest to colloidal particles in last years was renewed for semiconductor compounds due to quantum-size effects observed for optical and electrochemical properties of such particles when their size is comparable with the Bohr exciton radius (e.g., [1,2]). Colloidal systems with particles of different binary compounds was studied extensively (mainly,  $A^{\text{II}}B^{\text{VI}}$  and  $A^{\text{I}}B^{\text{VII}}$  semiconductor classes), and size-dependent features were indicated. They have the general character for direct-gap semiconductors and can be associated with the alteration of boundary conditions for charge carriers in small particles embedded in dielectric media. The colloidal-chemical synthesis is one of most useful methods of fabrication of similar particles. In contrast, more complex semiconductor compounds are produced usually by means of high-temperature syntheses when elements interact one with another attaining thermodynamic equilibrium. The latter is impossible under low temperatures in solutions. However, there is a feasibility of new compounds formation at the earlier steps of particle creation (nucleation and the beginning of lattice formation), when some instable phases can exist and species can possess increased reactivity [3].

In the report we present results of studies of ultrafine phases formation for a series of ternary  $A^{\text{I}}B^{\text{III}}C^{\text{VI}}_2$  compounds.  $\text{CuInS}_2$ ,  $\text{CuInSe}_2$ ,  $\text{CuGaS}_2$ ,  $\text{CuFeS}_2$ , and  $\text{AgInS}_2$  were synthesized in colloidal solutions (both aqueous and non-aqueous) and in polymer matrices. Size of particles was in the range of 2-10 nm, that revealed the pronounced quantum-size effects in optical properties. XRD and XPS evidenced on formation of the above chemical forms under certain conditions. In the result of partial oxidation (at the particle surface) a new absorption band in optical spectra centered in near-IR region appears which is specific for transition metal compounds due to charge transfer effects. Electronic structure of the  $A^{\text{I}}B^{\text{III}}C^{\text{VI}}_2$  particles comprise both quantum-size and chemical effects explicitly. The development of non-linear optical applications of these compounds in the form of ultrafine particles embedded in solid matrices (films, glasses) is in progress [4].

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### 84.A5 ADSORPTION OF PSEUDOISOCYANINE ON COLLOIDAL SILVER HALIDES PARTICLES

L. Jeunieu, Ph. Monnoyer, J. B. Nagy

*Laboratoire de Résonance Magnétique Nucléaire, Facultés Universitaires Notre Dame de la Paix,  
61, rue de Bruxelles, B-5000 Namur, Belgique*

The silver bromide particles are synthesized in the microemulsion AOT (sodium bis-2 ethylhexyl-sulfosuccinate)/Heptane/Water. The average diameter of the particles is  $\pm 50\text{\AA}$ . The molecules of pseudoisocyanine are replacing the molecules of the surfactant (AOT) on the surface of AgBr particles. The pseudoisocyanine, as other cyanines, form aggregates (called J-aggregates) on the silver halides particles. This causes an instability in the silver bromide dispersion. Indeed, a large part of the surface will be unprotected by the surfactant and the particles finally coalesce. The stability is however improved if the adsorption of cyanines is decreased. In this way, the particles will keep enough adsorbed molecules of surfactant for their stability. This can be achieved by conserving the particles at low temperature, or by using an inhibitor, p-xylene or by adding another surfactant which is more strongly adsorbed than AOT. The surfactant used is CTABr (Cetyltrimethylammoniumbromide). The amount of CTABr influences the stability of the particles and the size of the J-aggregates. If an appropriate amount of CTABr is used, the particles remain stable for 30 days after the adsorption of pseudoisocyanine.

The behaviour pseudoisocyanine (PIC) on silver chloride is drastically different. Indeed, PIC is desorbed as a function of time. The adsorption can be improved if the reaction is carried out at low temperature. This is opposite to the case of the AgBr where the adsorption was stopped at low temperature ( $-5^{\circ}\text{C}$ ).

## 85.A5 HYDROCARBON AND LIPID OXIDATION IN MICROHETEROGENIC SYSTEMS FORMED BY IONOGENIC SURFACTANTS AND/OR NANODISPERSED $\text{Al}_2\text{O}_3$ , $\text{SiO}_2$ and $\text{TiO}_2$

Kasaikina O.T.<sup>2</sup>, Kortenska V.D.<sup>1</sup>, Kartasheva Z.S.<sup>2</sup>, Kuznetsova G.M.<sup>2</sup>, Maximova T.V.<sup>2</sup>, Sirota T.V.<sup>1</sup>, Yanishlieva N.V.<sup>1</sup>

<sup>1</sup>*Institute of Organic Chemistry with Center of Phytochemistry BAS, Sofia, Bulgaria*

<sup>2</sup>*Institute of Chemical Physics RAS, Moscow, Russia*

The effect of ionogenic surfactants (AOT, SDS, CTAB) and microdispersed solid oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ) on the kinetics and mechanism of hydrocarbon (decane, dodecane, ethylbenzene, limonene,  $\beta$ -carotene) and lipid (sunflower oil methyl esters and triacylglycerols) liquid phase oxidation by molecular oxygen have been studied. The formation of reverse micro emulsions have been found in the course of the limonene autoxidation in the presence of surfactants by quasi-elastic light scattering method; the hydroperoxides formed affect the size of microemulsion particles. Surfactants and solid oxides were found to effect on the rate and mechanism of hydroperoxide decay. In the case of  $\beta$ -carotene oxidation when no hydroperoxide are formed the peroxy radical decay was found to be accelerated in the presence of reverse micro emulsion  $\text{H}_2\text{O}/\text{AOT}/n$ -decane that results the increase of the oxygen consumption. The effect of surfactant and solid oxides additives on the hydrocarbon (RH) oxidation and hydroperoxide (ROOH) decay depends on the RH nature, particle surface charge, and geometric factor. Anionic surfactant SDS forms coassociates with ROOH and catalyses the heterolytic decay of hydroperoxides. In the case of  $\alpha$ -phenyl ethyl hydroperoxide the SDS catalysed decay results phenol that is an acceptor of free radical. So the ethylbenzene oxidation is completely retarded in the presence of SDS. The same effect on ethylbenzene oxidation and ROOH decay was found to be caused by nanodispersed  $\text{Al}_2\text{O}_3$ . Anionic AOT gives stable reverse micelles and micro emulsions itself and due to hindered polar heads does not form coassociates with ROOH. By this reason AOT does not affect ROOH decay and RH oxidation rate. Cationic surfactant CTAB is found to be a catalyst for ROOH decay producing free radicals that cause the acceleration of RH oxidation. The effect of surfactants and cosurfactants on the inhibited oxidation of lipid and hydrocarbons depends on the nature of antioxidant used (phenols, aromatic amines, etc.).

## 86.A5 SYNTHESIS AND GROWTH MECHANISM OF MONODISPERSE $\text{GeO}_2$ PARTICLES IN AOT REVERSED MICELLES

Takeshi Kawai, Yuki Usui, Kijiro Kon-No

*Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo,  
Shinjuku-ku 1-3, Kagurazaka, Tokyo*

Monodisperse colloidal particles of various materials such as metal, metal carbonates and semiconductors have been prepared by using water droplets dispersed in reversed micellar systems. The physical and chemical properties of these particles, especially metal oxide particles obtained by hydrolysing the corresponding metal alkoxide, must be affected by the solubilized states of water<sup>1</sup>. In this paper,  $\text{GeO}_2$  particles are prepared by hydrolysing germanium tetraethoxide (GTE) in sodium 1,2-bis-2-(ethylhexyloxy)carbonyl-1-ethane sulfonate (AOT) reverse micelles as a function of  $R_w(=[\text{H}_2\text{O}]/[\text{AOT}])$ , and then the relationship between the formation of particles and the solubilized states of water is examined. Further, the growth mechanism of  $\text{GeO}_2$  particles is revealed by measuring the time dependence of turbidity, size and yield of the particles.

The solubilization region of water in isooctane solution of AOT could be divided into three realms, i.e., reversed micelle ( $R_w < 4$ ), swollen micelle ( $4 < R_w < 12$ ) and W/O microemulsion ( $R_w > 12$ ), depending on

the solubilized state of water revealed by NMR, ESR and Near-IR measurements<sup>2</sup>. Monodisperse particles were obtained in each realm and the sizes (50-1000 nm) increased with increasing  $R_w$ . The shapes of the particles were found to be spindle in the reversed and swollen micelles realms, but cubic in the W/O microemulsion realm. However, the structure of all the particles were crystalline  $\text{GeO}_2$  of  $\alpha$ -quartz form. In the case of W/O microemulsion realm of  $R_w=20$ , the turbidity of reaction solution appeared after about 5 min. SEM measurements showed that i) before 5 min spherical fine particles ( $<5$  nm) exist ii) in 5-60 min the size of  $\text{GeO}_2$  particles is greater with reaction time under the presence of the fine spherical particles. FT-IR measurements indicated that the hydrolysis of GTE is completed within 1 min and the yield of  $\text{GeO}_2$  gradually increase up to 60 min. Further, number of particles in a unit volume, which is calculated from the particle size and the yield, unchanged after 5 min. It can be concluded from these results that nuclei of  $\text{GeO}_2$  are formed by fusion of the fine particles and then  $\text{GeO}_2$  particles grow by adhesion of the fine particles. In another realm the growth mechanism was found to be the same except for the growth rate of  $\text{GeO}_2$  particles.

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## 87.A5 DEHYDROXILATION AND RE-HYDROXYLATION OF NANOSIZE SILICA PARTICLES. QUANTUM CHEMICAL MODELLING AND VIBRATIONAL SPECTRA VERIFICATION

V.D. Khavryutchenko<sup>1,2</sup>, V.M. Ogenko<sup>1</sup> and I.F. Mironyuk<sup>3</sup>

<sup>1</sup>Institute of surface Chemistry, National Academy of Sciences of Ukraine, Kiev, 252028 Ukraine

<sup>2</sup>Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, 141980 Russia

<sup>3</sup>Institute of Surface Chemistry, National Academy of Sciences of Ukraine,  
Kalush experimental factory, Ukraine

Dehydration and dehydroxilation of silica surface play an important role in flame silica particle formation and at the following heating treatment. To study these processes we have used supercluster approach in quantum chemistry. To calculate large silica particle clusters and sets of clusters we have used sophisticated semiempirical methods as AM1 and PM3. Each system was fully optimised and the force field and dipole moment derivatives have been evaluated too. The IR-spectra and neutron in elastic scattering spectra (INS) were used to verify computational models with experimental spectra both: infrared and neutron inelastic.

Dehydroxilation of silica surface particle was represented as a step-by-step process which included one water molecule formation from two nearest hydroxyl groups and extraction this water molecule from surface. New siloxane bond formation may be occurred in this process. After full optimisation this process was repeated up to full particle dehydroxilation. The size, structure and vibrational spectra (IR and INS both) for all dehydroxilation steps will be presented and discussed.

To investigate silica particle flame formation more complicated model was designed. Two silica clusters with different degree of dehydroxilations was included into space structure optimisation process. In case when silica surfaces contain only hydroxyl groups, the silica supercluster is formed with dipole-dipole interaction and H-bonding. In case when silica surfaces contain active centres like  $\text{Si}^+$  and  $\text{Si-O}^-$ , the whole particle formations are occurred.

To study the water influence on particle-particle interaction and vitrifying of high dispersed silica we have design some models using mechanochemistry capabilities of our software. We have studied the external force needs to move one silica cluster relative other with or without water molecule(s) between clusters. Details of cluster structures and their variation will be presented and discussed.

## 88.A5 LUMINESCENCE CHARACTERISTICS OF SILICON NANOCOLLOIDS

Keisaku Kimura, Shingo Iwasaki and Masayoshi Nakamura

*Department of Material Science, Himeji Institute of Technology Science Garden City,  
Kamigori, Akogun, Hyogo 678-12, Japan*

It has been reported that a highly oxidized porous silicon or nanocrystalline sample embedded in  $\text{SiO}_2$  matrix shows distinct blue-green photo-luminescence (PL) in addition to red-yellow luminescence. The origin of this blue-green PL seems no more clear than that of red-yellow PL. Thus the preparation of well-isolated particles is strongly required in order to elucidate the origin of visible PL from silicon nanostructures. Therefore much interest is focused on silicon colloid both from a technological and scientific aspect concerning its luminescent characteristic invisible region.

We have prepared silicon nanocolloids by trapping silicon nanocrystallites produced by a gas evaporation method combined with a matrix isolation technique into methanol or 2-propanol (99.9%). A glass chamber was evacuated to  $2.0 \times 10^{-6}$  Torr with a turbomolecular pump and then filled with methanol or 2-propanol vapor which had previously been degassed several times by a freeze and thaw technique. Under refrigeration, silicon nanocrystallites were prepared by the resistant heating technique and the formed nanocrystallites adhered to the surface of the frozen methanol or 2-propanol. The prepared silicon nanocolloid was yellow in color. We prepared five samples with different particle sizes from 3.7 to 9.8 nm by varying the pressure of the He gas from 0.5 to 5 Torr. Several sample treatment were tested as for the photoluminescence characteristics including air oxidation of the colloids and the alkaline treatment (NaOH, KOH and  $\text{Ca}(\text{OH})_2$ ). We have also made a surface potential measurement. Both the TEM image and the electron diffraction pattern show that the nanocrystallites are consistent with the diamond structure. The effect of surface oxidation on the luminescent characteristics was checked with two samples, fresh sample and one-day-old sample. The degree of oxidation of  $\text{SiO}_x$  was determined by the IR spectra, the value of  $x$  is estimated to be 1.2 for the fresh one and 1.7 for one-day-old one. In the UV-visible absorption spectra, the absorption edge shifts to high energy with the decrease of the average diameter from 9.8 to 3.7 nm, which is explained in terms of a quantum size effect. The spectra of the one-day-old samples were identical to those of fresh samples.

The broad PL emission band of the silicon nanocolloid appears at about 480 nm. This PL as so strong that the bright blue luminescent light from the sample was visible with naked eye even at room temperature. In the PL spectrum of the one-day-old silicon nanocolloid, we have found that the external quantum efficiency is increased from 0.06 % to 0.16 %. Since the results of the IR measurement show the increase of the degree of oxidation of the  $\text{SiO}_x$  layer in the old samples, the enhancement of blue PL is likely to be caused by the modification of the surface structure of the silicon nanocrystallites. The size-dependent shift of the UV-visible absorption edge implies that the electronic excitation is dominated by the electronic state of the silicon nanocrystallite affected by a quantum confinement, while the luminescence process seems to have a local nature bound to the interfacial region between the silicon nanocrystallite and the amorphous  $\text{SiO}_x$  layer. Hence blue PL may also be ascribed to a radiative recombination of excitons at a localization site near the interfacial region. Accordingly, we have dropped alkaline solids into silicon nanocolloid in order to chemically modify the electronic state of interfacial region. We have observed not only blue PL but also UV PL at room temperature. The broad PL band from the one-day-old sample modified with potassium hydroxide appears at about 350 nm and 480 nm, the latter is coincided with that of non-treated sample. We have found that the external quantum efficiency is increased from 0.16 % to 0.45 % at pH 9.0.

0.06% (fresh sample)  $\rightarrow$  0.16% (one-day-old sample)  $\rightarrow$  0.45% (alkaline treatment)

Above scheme summarizes a variation of the external quantum efficiency as a function of sample treatments. We have confirmed that cations do not affect UV PL, because the peak position or the spectral profile of the PL band hardly changed at all in dropping sodium hydroxide or calcium hydroxide instead of potassium hydroxide. The UV PL process seems to correlate with the SiOH bond or chemisorbed OH on the surface of silicon nanocrystallites.

## 89.A5 SYNTHESIS AND PROPERTIES OF NANOPARTICLES OBTAINED BY BOROHYDRIDE REDUCTION PROCESS

K. Klabunde<sup>1</sup>, I. Dragieva<sup>2</sup>, Z. Stoynow<sup>2</sup>

<sup>1</sup>Kansas State University, Dept. Chemistry, Kansas 66506, USA

<sup>2</sup>Bulgarian Academy of Sciences, CLEPS, Sofia, 1113 Bulgaria

The present review concentrates on the boron-containing nanoparticles, produced by the process of a chemical reduction of a metal salt solution with sodium borohydride.

Nanoparticles obtained from aqueous salt solution have a specific surface area ranging from 1 m<sup>2</sup>/g to 120 m<sup>2</sup>/g with a content of boron from 0.1 to 10 wt.% and a content of hydrogen from 0.01 to 2 wt.% in terms of the participation of one, two or more (including rare-earth) salts of metals.

Nonoparticles possess an amorphous structure and a spherical shape, without an oxide shelf, and contain boron atoms whose 1s electrons are connected by two types of binding energy (BE). Both states are quantitatively equal, especially in the magnetically disordered amorphous state and they also affect the catalytic role of the transition metal, increasing its electron donor functions or decreasing them by acceptance of electrons from one of the boron states.

By using aqueous salt solutions possessing the *trans*-structure of the corresponding aqua-complexes and changing the hydrodynamic by mixing the initial solutions, the particles obtained are nanocrystalline, angular, possessing smaller cell volumes and lattice parameters and a single value for BE of the B 1s electrons to the nuclei. The main fields of application for both type of nanoparticles have been discussed.

When non-aqueous solutions in diglyme were used, the reduction with NaBH<sub>4</sub> was carried out on cobalt, nickel, iron and copper ions, and as-prepared ultra fine particles of metals and metal borides were investigated for use in magnets, electronic, catalyst, etc. Some peculiarities of nanoparticles obtained from non-aqueous solutions and some specific techniques for their handling have been presented.

## 90.A5 RECOGNITION PHENOMENA IN POLYMER-COLLOIDAL METAL SYSTEMS

Ol'ga Ye. Litmanovich, Andrey A. Litmanovich and Ivan M. Papisov

Moscow State Automobile and Road Technical University, 64, Leningradsky Prosp.,

Moscow 125829, Russia

Polymer-metal nanocomposites were obtained via reduction of Cu<sup>2+</sup> in water solutions of poly (ethylene imine) (PEI) and poly (N-vinyl pyrrolidone) (PVP). Four systems were investigated.

i) In Cu-PVP system obtained composites include particles of Cu<sup>0</sup> with mean diameter 4-7 nm. The particles do not grow up on storage.

ii) In Cu-PEI system obtained composites include particles of Cu<sup>0</sup> with mean diameter 7-10 nm. The particles grow up on storage: after 6 days mean diameter reaches ~30 nm.

iii) If Cu<sup>2+</sup> reduction proceeds in simultaneous presence of PVP and PEI, the resulting composite includes only Cu<sup>0</sup> particles with mean diameter 4-7 nm which do not grow on storage. It means that growing Cu<sup>0</sup> particles do not 'see' PEI macromolecules and bind quantitatively with PVP.

iv) If PVP is added to the reaction mixture after the reduction of Cu<sup>2+</sup> in the presence of PEI is over, then two kinds of Cu<sup>0</sup> particles are observed after 6 days: with mean diameter 7- 10 and 30 nm. It means that PVP macromolecules partly replace PEI macromolecules in the initially formed composite; then, metal particles bound with PVP do not grow up, and those bound with PEI, do.

The results obtained are analyzed in the frame of theory of pseudo-matrix processes (I.M.Papisov *et al*, *Macromolecular Symposia*, 1996, v.106,pp.287-297). According to the theory, there are two steps of the process: (1) initial growth of metal particles without the contact with macromolecules, and (2) mutual 'recognition' of macromolecules and particles reached some 'critical' size accompanied by polymer-particle complex (PPC) formation and shielding of the surface of particles, the critical size being dependent on the nature of polymer and particles, as well as on the reaction conditions. If the shielding is effective enough, then the growth of particles is terminated (systems i and iii). If the shielding is not so effective, then the slow growth of particles is possible (system ii).

System iv demonstrates the possibility of substitution reactions characteristic for inter polymer interactions to proceed in metal containing PPC. Correspondence of theoretical picture for such reactions (A.A.Litmanovich and I.M.Papisov, *Polymer Science*, 1997, in press) to experimental data is discussed.

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## 91.A5

### CHEMICAL REACTIONS OF SILICA-COATED METALLIC NANOPARTICLES

Luis M. Liz-Marzán<sup>1</sup>, Michael Giersig<sup>2</sup>, Thearith Ung<sup>3</sup>, Paul Mulvaney<sup>3</sup>

<sup>1</sup>*Departamento de Química Pura e Aplicada, Universidade de Vigo, 36200 Vigo, Spain*

<sup>2</sup>*Hahn-Meitner Institut, Abt. Kleinteilchenforschung, 15109 Berlin, Germany*

<sup>3</sup>*Advanced Minerals research Centre, University of Melbourne, Parkville 3052, Australia*

The chemical reactivity of nanosized, silica-coated, gold and silver particles has been investigated using UV-visible spectroscopy and electron microscopy. It was found that both thin shells deposited from aqueous sodium silicate solutions and thicker shells formed by ethyl silicate hydrolysis in ethanol are porous, particularly to neutral reactants. Prolonged boiling of thicker shells (>30nm) strongly retards chemical reactivity by decreasing the porosity.

Silica coated gold does not dissolve in aqua regia, but both silver and gold particles dissolve in alkaline cyanide solutions, the rate depending on the silica shell thickness. This leads to formation of uniform, hollow nanosized silica nanoparticles.

The reaction of a single Ag@SiO<sub>2</sub> nanoparticle with I<sub>2</sub> to form AgI was monitored directly by transmission electron microscopy. It was observed that AgI was generated both as a core and as a surface product. This is attributed to silica shell rupture due to the growth of AgI in the silica pores.

## 92.A5

### SIZE CONTROL OF CdS MICRO-FINE PARTICLES DISPERSED IN POLYMER FILMS

Yoshikazu Miyake, Makoto Umesawa, Yoshio Hashimoto and Minoru Yoshida

*Kansai University, Faculty of Engineering, Department of Chemical Engineering, 3-3-35 Suita city, Osaka, 564, Japan*

In this study, we prepared the polymer films dispersed CdS micro-fine particles by the two different methods. The diameter and the size distribution of CdS fine particles were determined from the spectra of the UV and visible wave length by taking into accounts of the size dependence of the band gap, which was estimated by the some models.

First method is the use of the complex coacervation, which is used to prepare microcapsule. Polyacrylic acid (PAA) as anion hydrophilic polymer and polyallyl-amine (PAAM) as cationic one were used as stabilizer. The diameter of CdS fine particles in the presence of PAA was smaller than that in the presence of PAAM. It is inferred that this behaviour is caused by the interaction between Cd<sup>2+</sup> ion and anionic polymer, which is observed by the titration and dynamic light scattering. When the CdS fine particles prepared in the presence of both stabilizers were mixed, the complex coacervation occurred and prepared the polymer film. But the fine CdS particles precipitate on the film surface and the polymer film dispersed CdS fine particles could not be obtained by this coacervation method. On the other hand, the polymer film dispersed CdS micro-fine particles is prepared with the mixing of the anionic hydrophilic polymer containing Cd<sup>2+</sup> and the cationic hydrophilic polymer containing S<sup>2-</sup>. These behaviour of the coacervation will be discussed from the measuring the mobility of the coacervation by the use of the electrophoresis light scattering. The size of CdS micro-fine particles were controlled by the concentration of the hydrophilic polymer stabilizer and the kinds of S-atom sources.

Second method is the use of the microemulsion stabilized by surfactant in monomer solutions, which is used methyl methacrylate. Cadmium ion is solubilized in microemulsions by the use of the sodium bis (2-ethylhexyl) suiphosuccinate (AOT). The microemulsion size was controlled by the change of

$W_0 = [H_2O]/[AOT]$ . The polymer film was prepared by the polymerization of methyl methacrylate solvilinearized  $Cd^{2+}$ . Then, the film was maintained in the atmosphere of  $H_2S$  vapor and the micro-fine particles of  $CdS$  dispersed in the polymer film was obtained. The size of  $CdS$  was controlled by  $W_0$ .

### 93.A5 FORMATION AND STABILITY OF COLLOIDAL GOLD PRODUCED FROM CHLOROauric ACID BY CITRIC ACID

Yasushige Mori<sup>1</sup>, Yoshihisa Murao<sup>1</sup> and Yoshikazu Miyake<sup>2</sup>

<sup>1</sup>Dept. of Chem. Eng. & Mater. Sci., Doshisha University, Kyotanabe, Japan

<sup>2</sup>Dept. of Chem. Eng., Katsai University, Suita, Japan

The formation of colloidal gold produced from chloroauric acid by the reducing agents, such as hydrazine, citric acid and 1,3-acetone dicarboxylic acid, was studied by using a spectrophotometer. The absorption to the gold sol appeared in the range of the wavelength from 500 to 600 nm. When tri-sodium citrate was used as a reducing agent, the color of the old sol solution was changed deep purple before turning red. Colloidal gold prepared in this condition was very stable. The wavelength at the maximum absorption increased with the particle size of the gold sol measured by a small angle X-ray scattering and a dynamic light scattering.

The rate of sol formation could be estimated by the absorbance at 525 nm wavelength, at the condition used citrate acid or tri-sodium citrate to reduce chloroauric acid, of which concentration was below 0.24 mM. This rate increased with decreasing pH value. It indicated that the di-hydrogen citrate ion might play the important role of the reduction of chloroauric acid, and that the adsorption of citrate ion on the surface of the gold sol might prevent the growth of particles. The induction period, which was concerned with the period of the gold cluster formation, increased with the concentration of chloroauric acid. It could be concluded that the length of the induction period is related to the concentration of chloride ion, together with the experimental results of the dependence of sodium chloride concentration. The particle size decreased with increasing the concentrations of hydrogen citrate ion and chloroauric acid. Therefore, the size of gold sol could be controlled by the concentrations of chloroauric acid and citric acid, and pH value related to the dissociation of citric acid. The stability of colloidal gold depended on pH value, which could be related to the concentration of citrate ion. The addition of sodium hydroxide after formation of colloidal gold would be a suitable method to make a stable gold sol, because the citrate ion works as the stabilizer to absorb to the surface of gold sol.

### 94.A5 SELF-ASSEMBLY OF SUB-MICRON ANNULAR RINGS FROM SOLUTIONS OF NANOPARTICLES

Pamela C. Ohara and William M. Gelbart

Department of Chemistry & Biochemistry, University of California, Los Angeles, USA

Ordered arrays, or superlattices, of semiconductor and metal nanocrystals represent a promising new class of materials. We previously reported the formation of two dimensional annular ring like arrays from solutions of large (3-6 nm diameter), fairly monodisperse, organically-passivated metal particles. The structures were identified by transmission electron microscopy, and are characterized by nearly perfect rings whose annular widths are small compared to their diameters (~0.1-1 microns). We present here a theoretical mechanism that shows how these configurations are accounted for in terms of the evaporation of -- and hole nucleation in -- wetting thin liquid films, and the forces exerted on particles along the rims of opening holes. Each annular ring consists of close packed nanoparticles, and is formed upon the pinning of the contact line of a growing hole which nucleates in sufficiently thin films of dilute solutions of the particles. Our mechanism treats the effects of particle size and concentration. Ideas are also tested via a dynamic Monte Carlo simulation, which demonstrates the effects of the relevant time scales of fluid flow and evaporation on the resulting configurations.



## 95.A5 INVESTIGATION OF THE STRUCTURE AND STABILITY NATURE OF NANOPARTICLES TiO<sub>2</sub> HYDROSOLS

O.B. Pavlova-Verevkina, V.V. Nazarov, A.V. Pertsov  
Karpov Institute of Physical Chemistry, Moscow, Russia

TiO<sub>2</sub> hydrosols were prepared by the hydrolysis of Ti tetrabutylate (TiTB) and Ti methylcellosolvate (TiMC) with HCl as stabilizer. The stable sols were formed spontaneously at the room temperature by mixing of alcoholate, water, alcohol and acid in the certain ratios. The conditions of the alcoholate-precursor hydrolysis were varied by changing of the sequence of the reagents mixing. Complex investigation of colloidal properties (viscosity, turbidity, Raman spectra, pH, main radius and charge of the particles, thresholds of coagulation by electrolytes) of the sols and of the structure of xerogels, obtained by drying these sols, was carried out.

The sols with the same chemical composition prepared in different ways from TiTB were found to have similar colloidal properties. It means that sizes and structure of primary particles in these sols do not depend on the synthesis conditions and hence these sols have the equilibrium nature. X-Ray diffraction patterns of the xerogels prepared from these sols were also practically identical and contained a set of broadened peaks corresponding to TiO<sub>2</sub> anatase modification. The main size of the anatase crystallites, estimated through broadening of the peaks, was equal to 6-9 nm. On the contrary, the sols prepared in different ways from TiMC had different properties. Thus, if in the course of the hydrolysis the system evolved only through homogeneous states (without formation of gel or solid oxide phases) the formed sol was similar to the equilibrium sols, obtained from TiTB. If the hydrolysis of TiMC included formation of heterogeneous states, the sols obtained were less stable and had hybrid structure: besides the nanometer anatase crystallites they also contained polymeric aggregates. Kinetics and mechanism of the coagulation of the sols with different structures by electrolytes were studied.

The sols, close to the equilibrium state, were shown to coagulate reversible after adding some electrolytes. Xerogels, obtained from these sols by drying at the room temperature, dispersed spontaneously in water. These features seem to be due to the large hydrated layer on the surface of oxide particles.

## 96.A5 CADMIUM SULFIDE NANOPARTICLES PREPARED IN WATER AND IN WATER-IN-OIL MICROEMULSION

S. Peretz<sup>1</sup>, Mihaela Olteanu<sup>2</sup> and Otilia Cinteza<sup>2</sup>

<sup>1</sup>Institute of Physical Chemistry, Department of Colloids, Spl. Independentei 202,  
78202, Bucharest, Romania

<sup>2</sup>University of Bucharest, Department of Physical Chemistry, Blvd. Republicii 13, Romania

Cadmium sulfide nanoparticles were prepared by mixing two reverse micellar solutions with the same water content value,  $w_o = [H_2O]/[ANT]$ , in the range 6-12. In this work we use a lot of stabilizers like: styrene/maleic anhydride copolymer ( $M=50,000$ ), vinyl acetate/maleic anhydride copolymer ( $M=100,000$ ;  $222,000$ ) and sodium polyacrylate ( $M=40,000$ ) in alkaline medium. Using the same stabilizers, the nanoparticles were made in aqueous medium in a similar range of CdS concentration with those obtained in microemulsion system. The band gap,  $E_g$ , for the nanoparticles obtained in microemulsion and in aqueous medium was determined by fitting the absorbance data of the visible spectrum with the Wang equation [1], and the diameters of particles can be estimated using Brus's equation [2]. We have found that for the same diameter, the band gap ( $E_g$ ) in microemulsion system is greater than obtained in water. The stability in time for the CdS particles in aqueous medium is greater than found in microemulsion, in presence of the same stabilizer. Among all the stabilizers, the best was styrene /anhydride copolymer in aqueous medium and in microemulsion system.

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## 97.A5 COLLOIDAL ASSEMBLIES USED TO MAKE NANOSIZED PARTICLES DIFFERING BY THEIR SIZE AND SHAPE

M. P. Pileni

*Laboratoire S.R.S.I., U.R.A.C.N.R.S. 1662, Université P. et M. Curie (Paris VI), B.P.52,  
4 Place Jussieu, F-75231 Paris Cedex 05, FRANCE, and C.E.A.-C.E.N. Saclay,  
DRECAM-S.C.M. F-91191 Gif-sur-Yvette, Cedex, France*

In this paper we will demonstrate that self assemblies is a good model to mimic biomineralization processes. Syntheses of nanoparticles in water in oil and oil in water micelles permit to control the size of the particles. When the syntheses are performed in lamellar phase or in interconnected cylinders, cylinders are obtained. The length of these cylinders depends on the structure of the assemblies. In lamellar phase very large cylinders (1  $\mu\text{m}$  rod) are formed whereas in the interconnected assemblies, the length of the cylinders is smaller (20 nm).

The nanoparticles studied are copper metallic particles, cobaltferrite, magnetic semiconductors.

In some cases, the polydispersity in size is so small that the particles are able to arrange themselves in either monolayer organized in a hexagonal network or in three dimensional superlattice forming a "pseudo" crystal organized in a centred cubic face.

## 98.A5 DEVELOPMENT AND COMPARISON OF METHODS FOR THE FRACTIONATION OF MAGNETIC NANOPARTICLES

T. Rheinländer<sup>1</sup>, W. Weitschies<sup>1</sup>, R. Kötz<sup>2</sup>, W. Semmler<sup>1</sup>

<sup>1</sup>*Institut für Diagnostikforschung GmbH, Spandauer Damm 130, D-14050 Berlin, Germany*

<sup>2</sup>*Physikalisch-Technische Bundesanstalt, Abbestrasse 2 -12, D-10587 Berlin, Germany*

Ferrofluids are colloidal dispersions of stabilised ferro- or ferrimagnetic nanoparticles. They are widely used, e.g. as damping material for loud speakers, for the separation of material or as injectable contrast agents in magnetic resonance imaging.

Depending on their application different magnetic properties of the nanoparticles within these ferrofluids are required. Usually there is a broad distribution of the magnetic parameters of the particles. Therefore very often only a small fraction of the particles contributes to the desired effect. In order to optimise ferrofluids we developed two different methods for the fractionation of ferrofluids and compared the obtained fractions of magnetic nanoparticles regarding to particle size and magnetic parameters.

Size selective fractionation of iron oxide particles in water was achieved by size exclusion chromatography. Investigations of the fractions showed that the magnetic quantities like moment or initial susceptibility increase with the particle diameter.

Additionally a novel magnetic fractionation method was developed. The fractions obtained by this method show an increase of the magnetic parameters with the particle diameter like in case of the size exclusion chromatography. This is quite remarkable since the two methods rely on different separation mechanisms. The magnetic fractionation exhibits considerable advantages (faster, without additives, etc.) over the size exclusion chromatography.

Some of the fractions obtained are useful, e.g. one with larger particles for magnetic separation.

## 99.A5 COLLOIDAL DISPERSIONS OF MICROPOROUS MATERIALS: SYNTHESIS AND NUCLEATION/GROWTH MECHANISMS

B. J. Schoeman and J. Sterte

*Department of Chemical Technology, Luleå University of Technology, S-97187 Luleå, Sweden*

Microporous materials are utilized within commercially important areas as catalysis, washing detergent industry and in separation, adsorption and sensor technologies. An important class of microporous

materials is the group of molecular sieves - crystals with well defined channel geometries in the angström range. This attractive property allows for size and shape selective separations on the molecular level. Several applications in which molecular sieves play an important role require that the crystal size be in the colloidal size range. For example, in diffusion limited catalysis, ion-exchange and pore mouth catalysis, high external surface areas and short diffusion paths allow not only for increased activity but radically influence product selectivity. In sensor applications, greater mass responses and short response times are considered possible.

Several molecular sieves have been synthesized in this laboratory in the form of stable colloidal dispersions in which the average crystal size is less than 200 nm. The synthesis of discrete colloidal molecular sieve crystals is exemplified using the nominally all-silica crystalline tetrapropylammonium (TPA) silicalite-I (chemical composition  $(\text{TPA})_2\text{O} \cdot 48\text{SiO}_2 \cdot \text{H}_2\text{O}$ , orthorhombic symmetry, channels of intersecting 10-member rings  $5.7 \times 5.1 \text{ \AA}$  and  $5.4 \text{ \AA}$ ). Clear precursor sols with the molar composition 9 TPAOH 25  $\text{SiO}_2$  480  $\text{H}_2\text{O}$  100 ethanol are prepared by adding a TPAOH solution to tetraethoxysilane whereafter the two immiscible phases are hydrolysed at room temperature. The precursor is hydrothermally treated with reflux at 100 °C for 48 h whereafter a colloidal dispersion containing discrete crystals with an average size of 95 nm (as measured by dynamic light scattering) is obtained. Excess TPAOH and unreacted  $\text{SiO}_2$  is removed in the following purification process.

Molecular sieve nucleation and growth mechanisms have been studied using TPA-silicalite-I as the model system. This study consists of two parts. (i) The clear precursor sol described above has been characterized with respect to the particulate material present in suspension prior to hydrothermal treatment by FI-ir, FI-Raman, cryo-TEM and high effect laser light scattering. The results of these studies show that siliceous sub-colloidal particles with an average size of 2.6 nm exist in suspension. The particles are not simply amorphous siliceous particles but rather, they possess a structure with a degree of order such that they may be considered being zeolitic nuclei. This is the first report in the literature dealing with the identification and characterization of such precursors. (ii) Hydrothermal treatment of the clear precursor sols result in the crystallization of colloidal TPA-silicalite-I crystals as described above. A high temperature *in-situ* high effect laser dynamic light scattering study was performed to establish the relationship between the sub-colloidal particles and the well crystallized TPA-silicalite-I. The entire initial crystallization stage (crystal size range 2-30 nm) could be monitored. The results show quite clearly that a second particle population appears in suspension besides the sub-colloidal particle fraction - the latter is present throughout the course of crystallization. Of particular interest is the very initial stage of hydrothermal treatment. A closer study of this stage yields the result that certain sub-colloidal particles (probably the largest in the particle size distribution) increase in size upon hydrothermal treatment while the remaining subcolloidal particles serve as a nutrient reserve for the growing crystals. The role of the sub-colloidal particles as zeolitic nuclei confirms the results obtained above in the first part of the study.

## 100.A5 DYNAMICAL BEHAVIOUR OF CO ADLAYER ON SILICA SUPPORTED Pd AND Pd-Au NANOPARTICLES

N.V. Serebryakova

*Institute of Physical Chemistry, Russian Academy of Sciences, Leninskij prosp. 31, Moscow, 117915 Russia*

In this work CO chemisorption on silica supported Pd and Pd-Au nanoparticles were investigated with respect to particle size, coverage, and substrate temperature by Fourier Transform Infrared spectroscopy. Particle size was varied by initial compound nature and concentration as well as subsequent sintering of supported substances and hydrogen treatment conditions. Mean particle diameter and size distribution were determined by High Resolution Electron microscopy.

Substantial difference of adlayer behaviour was observed depend on particle size. In the case of Pd particles with diameter > 5 nm, as it can be seen from the spectra, initial Pd surface is presumably {110} and this surface is transformed by enhanced CO coverage at 300 K likely monocrystal Pd {110} surface in the work [1]. Namely, Pd surface undergoes adsorbate-induced reconstruction at immediate coverages and it is observed very complex mixed adlayer structure at high coverages, that it might be interpreted in accordance with [1]. For Pd-particles with diameter < 4 nm, initial {110} surface structure is more stable: the single symmetric band of stretch vibration for adsorbed CO with relatively narrow band width centred at

1890  $\text{cm}^{-1}$  is observed in wide coverage range. Its actual FWHM is about only 70  $\text{cm}^{-1}$ , in contrary with 200  $\text{cm}^{-1}$  and more usually observed for supported Pd. The spectral sequencies are not change dsignificantly, when the dilution of Pd atoms by 25% Au atoms take place:only band intensityis a little diminished, and the band is broadened, to 90  $\text{cm}^{-1}$ . However, desorption temperature is decreased.

It should be pointed, that bands observed arc more broad in comparison with monocrystal Pd {110}, where FWHM only 23-27  $\text{cm}^{-1}$  was determined [1]. With aim to understand a cause of CO band broadening on Pd and Pd-Au nanoparticles, the influence of substrate temperature on the spectra of adsorbed CO has been studied. It has been stated, that temperature decrease from 300 to 100 K result in sufficient narrowing of CO band (more than in 0.3) without substantial shift of the band maximum. Such behaviour is not observed usually on massive metals, and it is evidencied in favour of strong dynamical interaction between adsorbed CO and nanoparticle surface as one from the causes of band broadening.

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## 101.A5 ENZYME ENTRAPPED INTO THE POLY(N,N-DIALLYL-N,N-DIDODECYL AMMONIUM BROMIDE)/AEROSOL OT NANOCAPSULES

Yu.E. Shapiro, E.G. Pychteeva

*Bogatsky Physico-Chemical Institute, National Academy of Sciences, Odessa, Ukraine*

A high catalytic activity of enzymes, their ability to realize the chemical processes under mild conditions, and the matchless selectivity of an action open up broad prospects for use of the biocatalysis in processes of the fine organic synthesis. However, enzymes show these rare properties only in an aqueous solution within the close ranges of pH and temperatures. The transition from water as a reaction medium to an organic solvent, or going out the optimal pH and temperature ranges in aqueous phase are accompanied either by the enzyme denaturing or by the dramatic drop of its catalytic activity by the disappearance of the substrate specificity. One can escape this trouble fully or partly through a creation of the water or organic soluble biocatalytic systems such a senzymes entrapped into liposomes or nanocapsules.

The purpose of this work was an immobilization of the native  $\alpha$ -chymotrypsin within nanocapsules from reversed hydrated micelles of UV-polymerized N,N-diallyl-N,N-didodecyl ammoniumbromide, DDAB, in cyclohexane ( $w_0 = [\text{H}_2\text{O}]/[\text{DHAB}] = 22 \text{ mol/mol}$ ). These biocatalytic systems may act both in an organic solvent and in an aqueous phase after precipitation by acetone and further addition of AOT. In this case the unilamellar liposomes are formed. They have the inner monolayer from the poly-DDAB network, and the outer monolayer, from the AOT molecules. An enzyme globule remains as encapsulated in the inner water cavity of a vesicle. The alterations in IR- and  $^{13}\text{C}$ -NMR spectra of the UV-irradiated dispersions make it possible to control the emulsion polymerization degree. This one is equal to 70% of monomer DDAB. According to the light scattering data the average outer diameter of nanocapsules is 20 nm.

The nanocapsular form of  $\alpha$ -chymotrypsin has been used for study of the enzymatic activity by the p-nitrophenyl acetate hydrolysis. It has been shown using the integral form of the Michaelis-Menten equation, that by encapsulation of  $\alpha$ -chymotrypsin the values of Michaelis constant,  $K_m$  do not change. However the values of  $V_{\max}$  and product inhibiting,  $K_P$ , constants decrease at 3, and 1.6 times correspondingly.  $\alpha$ -Chymotrypsin entrapped into nanocapsules has the high thermostability keeping one's own activity up to 80°C. The polymer network blocks conformational transitions of an enzyme molecule by heating of a system.

## 102.A5 NANOSTRUCTURAL COMPOSITES OF CADMIUM AND ZINC SULPHIDES INCORPORATED IN SILICATE MATRICES BY SOL-GEL TECHNIQUE

N.P. Smirnova<sup>1</sup>, A.M. Eremenko<sup>1</sup>, A.I. Kryukov<sup>2</sup>, A.V. Korzhak<sup>2</sup>, S.A. Kuchmii<sup>2</sup>

<sup>1</sup>*Institute of Surface Chemistry National Acad of Sci. of Ukraine, 252022, Pr. Nauki 31, Kiev, Ukraine.*

<sup>2</sup>*L.V.Pisargevskii Institute of Physical Chemistry National Acad. of Sci. of Ukraine, 252022, Pr. Nauki 31, Kiev, Ukraine.*

Investigation into the properties of nanosized colloidal particles of semiconductors has indicated that they typically display a higher photocatalytic activity than that of routinely used polycrystalline or supported materials of the same composition. In this connection it is seen as rather critical to seek ways of creating dispersed porous materials within whose bulk there are distributed semiconductor nanoparticles stabilised more safely than in colloidal solutions and capable, due to well-developed pore system of interacting with liquid organo-phase reagents. This work is devoted to the sol-gel synthesis of CdS/SiO<sub>2</sub> and ZnS/CdS/SiO<sub>2</sub> microheterogeneous systems and investigation their optical and photocatalytic properties. CdS and CdS\*ZnS particles included into silica matrix were prepared by adding of Cd and Zn salts into initial solutions to provide the tetraethoxysilane hydrolysis followed by precipitation of sulphides just after silica gelation. CdS/ZnS ratio was 1/3 for all samples. The blue shift of adsorption edge for the all samples is observed as a result of size quantization effect due to the formation of the semiconductor nanoparticles in silica matrix.

Catalytic activity of synthesized systems was examined in reaction of hydrogen production from sulphide solutions. Efficiency of hydrogen photoproduction was found to depend on semiconductor concentration. It can be explained as a result of size quantisation effects and alteration of optical transmission of visible light through ZnS layer to the interface between ZnS and CdS and suppression of CdS interaction with electron-donor. Then microheterogeneous systems prepared by sol-gel method are stable and their optical and photocatalytic properties remained unchanged during a year.

## 103.A5 FORMATION OF TiO<sub>2</sub> MESOPOROUS FILMS USING REVERSE MICELLES AS PRECURSOR SOLUTIONS

E. Stathatos<sup>1</sup>, P. Lianos<sup>1</sup>, F. Del Monte<sup>2</sup>, D. Levy<sup>2</sup>, D. Tsiourvas<sup>3</sup>

<sup>1</sup>*University of Patras, Engineering Science Dept., 26500 Patras, Greece*

<sup>2</sup>*Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain*

<sup>3</sup>*NCSR "Demokritos", Institute of Physical Chemistry, 15310 Athens, Greece*

TiO<sub>2</sub> mesoporous films have been made by hydrolysis of titanium isopropoxide in reverse micellar solutions of either AOT or Triton X-100 in cyclohexane, followed by dip-coating and heating to 450°C. The obtained mesoporous structure is characterized by a remarkable size and shape monodispersity of the constituent titania particles. The procedure involves three stages: (1) the reverse micelles are made by mixing of cyclohexane, surfactant and water. Several combinations have been tested but optimal conditions were obtained for surfactant concentration equal to 0.2M and water concentration equal to 0.4M. Titanium isopropoxide was then added under stirring at concentration 0.2M. Immediately after alkoxide addition, gelation begins, by TiO<sub>2</sub> polymerization, which is faster in the case of AOT; (2) a glass slide, cleaned in sulfochromic solution, rinsed in Millipore water and dried under N<sub>2</sub> flow, is dipped in the gel at an early stage of gelation, i.e. a few minutes after addition of alkoxide. The obtained composite surfactant/inorganic film is uniform and transparent. Attachment of the film on the glass slide is possible not only for the ionic AOT but also for the non-ionic Triton X-100, thanks to the TiO<sub>2</sub> polymer network that strongly attaches to the underlying substrate material through -Si-O-Ti-bonds; finally, (3) the composite film is slowly heated up to 450°C, so that the organic content is burned out to yield a TiO<sub>2</sub> mesoporous film. The material obtained in each one of the above three stages, i.e. the reverse-micellar solution, the gel, the composite film and the TiO<sub>2</sub> film are very interesting physicochemical systems by themselves. The variants of each system affect the properties of the system obtained in the next stage thus providing control for the properties of the final product. We have studied each material by employing fluorescent probing methods for the reverse micelles,

the gel and the composite film, and SEM, TEM and AFM for the  $\text{TiO}_2$  film. The fluorescent probes are introduced in the original solution before alkoxide addition.

## 104.A5

### SIZE, HYDRATION AND PRESSURE EFFECTS IN NANOCLUSTER SYSTEMS

I. P. Suzdalev, Yu. V. Maksimov, V. N. Buravtsev

*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Russia.*

For nanocluster region of the matter there appear new properties compared to that in the atomic dispersions and in the massive materials. Indeed, atomic and molecular electronic terms change dramatically upon transition from atomic dispersion to a solid state. Moreover, collective phenomena such as lattice dynamics, conductivity and magnetism are prerogatives of the solids. These phenomena are, in turn, strongly affected by the size effects.

Two groups of size effects are considered for iron oxide cluster systems: intracluster dynamics connected with melting of the cluster and magnetic phase transitions in clusters. The following cluster systems were under study: (1) ferrihydrite clusters isolated in pores of polysorbates, (2) gamma iron oxide clusters non-modified by carbon inclusions, (3) gamma iron oxide clusters modified by carbon inclusions and (4) oxyhydroxide clusters isolated in pores of sulphonated exchange resin.

For nanoclusters (1) and (2), an increase in intracluster atomic mobility was observed upon reaching critical size of clusters ( $d \sim 2\text{-}3\text{nm}$ ). This effect was discussed by thermodynamic approaches taking into account quantum effects of fluctuation between solid and liquid states, change of cluster surface energy, change in chemical potential and drop in melting point typical of small clusters. Intracluster atomic mobility was shown to increase by the action of surfactants.

Ordinarily the isolated magnetic clusters lose the magnetic ordering by second order magnetic phase transitions or by super paramagnetic behavior when the magnetic moment of a cluster fluctuates as a whole. Both cases give rise to the smooth temperature dependence of magnetization. The association of nanoclusters in the nanocluster systems changes insignificantly the character of these curves.

Besides the second order magnetic phase transitions in nanoclusters, the first order magnetic phase transitions were observed in nanocluster systems (1), (3) and (4). This phenomenon was interpreted by thermodynamic approaches in terms of the first order magnetic phase transition in nanoclusters or the jump-like magnetic transition (JMT). The JMT was shown to be very sensitive to the surface energy, cluster-cluster, cluster-support interactions, magnetostriction and cluster compressibility. There were predicted the appearance of new properties of the matter at the point of association of isolated nanoclusters into a nanocluster system. The new properties may also arise under the action on clusters of external pressure and hydration of the matrix.

The thermodynamic approach introduces the critical parameters of the system suffering the effect of JMT: critical size ( $d_{\text{CR}}$ ) of a cluster and temperature ( $T_{\text{CC}}$ ) at which the cluster system loses magnetic ordering by the jump. For nanocluster systems (1) and (3) the following critical parameters were obtained by Mössbauer spectroscopy:  $d_{\text{CR}} \sim 3\text{nm}$ ,  $T_{\text{CC}} \sim 7\text{-}10\text{K}$  and  $d_{\text{CR}} \sim 12\text{nm}$ ,  $T_{\text{CC}} \sim 200\text{-}300\text{K}$ , respectively. These values are in a rather good agreement with the thermodynamic predictions.

For clusters (4), the hydration of polymeric matrix was shown to shift the critical temperature of magnetic phase transition by ca.  $3\text{-}4\text{K}$ . This effect was interpreted in terms of variation of the extent of cluster-support interaction changing surface energy of the cluster. For relatively large clusters (3) with  $d \sim 12\text{nm}$ , the shift of the critical temperature for the JMT was treated in terms of the lattice strain (pressure) induced by carbon inclusions.

## 105.A5 THE OPTICAL PROPERTIES OF ALIGNED COLLOIDAL GOLD RODS

Bianca M.I. van der Zande

*Philips Research Laboratories, Eindhoven, The Netherlands*

*Van 't Hoff Laboratory for Physical and Colloid chemistry, Utrecht University, Utrecht, The Netherlands*

*Advanced Mineral Products Research Centre, University of Melbourne, Melbourne, Australia*

Anisotropic metal particles dispersed in a liquid are of interest owing to their tendency to align in external fields e.g. electric, magnetic, mechanical or rheological fields, resulting in a change in optical properties. By combining electrodeposition in nanopores with colloid chemistry, a stable dispersion of gold rods can be obtained [1]. The aqueous gold rod dispersions exhibit an interesting absorption behavior, which strongly depends on aspect ratio. Due to the anisotropy, the absorption spectrum of randomly orientated colloidal gold rods comprises of a longitudinal and a transverse resonance contribution.

By aligning the gold rods by means of an external field, the absorption behavior will change. It is possible to eliminate one absorption peak using polarised light. Using unpolarised light results in a decrease or increase in the absorption, because alignment induces either a decrease in cross section or increase in cross section, respectively. In this talk the optical properties of colloidal gold rods in random orientation as well as in aligned orientation of the aspect ratio and field strength will be discussed as function.

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## 106.A5 PREPARATION OF MnO<sub>x</sub> NANO-PARTICLES VIA HYDROLYSIS OF MANGANESE COMPLEXES

A.D. Zarlaha and P.J. Pomonis

*Department of Chemistry, University of Ioannina, Ioannina 45110, Greece*

Nano-particles with dimensions from 1-1000nm often possess significantly different physical and chemical properties from those of the massive materials. In recent years there is an extensive research on such particles because of their increasing technological importance in a wide area of applications such as magnetic recording media, medical diagnostics, ceramics, paints and catalysts. For these reasons a variety of methods have been proposed for their synthesis. The selection of the synthetic method depends on the final use of nano-particles [1]. In this work we present the synthesis of manganese containing nanoparticles via a novel method of hydrolysis of multinuclear complex of this metal [2].

The complex used was trinuclear one having the formula  $[\text{Mn}_3(\text{CH}_3\text{OO})_6(\text{pyr})_3]\text{ClO}_4$  [2,3]. Its synthesis route was similar to that followed in [2,3] and took place in non aquatic media because of its sensitivity to water. In order to prepare the nanoparticle material the complex was hydrolysed carefully at constant rate and simultaneous measurement of pH. As a result a brown precipitate was obtained. This was separated by centrifugation and dried at 110°C for 24 hours. The hydrolysis was performed in various conditions, namely ultrasonic environment, increased temperature (40°C), presence of organic solvents and as well as the presence of Li, Fe, La, Mn, Ni, Co cations in the form of acetate and nitrate solutions. The obtained materials were dried at different temperatures (100-700°C) and the determination of the surface area and the pore volume took place by using the single-point BET method of N<sub>2</sub> adsorption as well as by N<sub>2</sub> adsorption-desorption isotherms determined at 100,200,300,400°C in an N<sub>2</sub> porosimeter. The original materials obtained were examined for their thermogravimetric behaviour in a thermobalance.

The results, showed that the particles possess a high surface area 200-400 m<sup>2</sup>/g in the range of 200-400°C depending on the hydrolysis conditions. In the temperature range 500-700°C the ssa drops to 50 m<sup>2</sup>/g. Very high surface area materials were obtained when hydrolysis took place of cations.

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## 107.A6 STABILITY OF SILICA PARTICLES IN SURFACTANT PHASES

V.L. Alexeev<sup>1</sup>, P. Ilekci<sup>2</sup>, B. Cabane<sup>2</sup>

<sup>1</sup>Petersburg Nuclear Physics Institute, Condensed State Research Division, 188350, Gatchina, Russia

<sup>2</sup>Equipe mixte CEA-RP, Service de Chimie Moléculaire, CE-Saclay, 91191 Gif sur Yvette, France

Colloidal dispersions are stabilized by repulsions that keep the dispersed particles apart from each other. In water, the repulsions often originate from the overlap of counterions clouds that surround each particle. These repulsions are established during the synthesis of the particles. However, the aqueous media in which the particles are synthesized are often not the medium required for applications. For instance, it may be desired to disperse the particles in a different aqueous phase (different ions and pH), in a nonaqueous solvent, or else in a polymer matrix. Then the difficulty is to maintain the stability of the dispersion during the solvent exchange and in the final dispersing phase.

We describe the transfer of mineral negatively charged particles exemplified by silica to surfactant phases exemplified by Triton X100 and C<sub>12</sub>E<sub>4</sub>. The interactions of nonionic surfactants with mineral surfaces are well understood; in dilute dispersions it is known that surfactant micelles adsorb on the mineral surfaces [1,2]. Our aim was to use this adsorption to produce silica particles that would be covered with micelles. The expectation was that the adsorbed micelles would act as "bumpers" between particles preventing any direct contact between them. In this way the particles could not segregate from the surfactant phase and would remain dispersed in it.

We have demonstrated [3] that with a nonionic surfactant that forms micelles (Triton X100), dilute silica dispersions have enhanced stability if the silica particles are fully covered with adsorbed surfactant micelles. Concentrated dispersions are also stable provided that the particles remain separated by at least one layer of micelles. Beyond full coverage, excess micelles may cause depletion flocculation of the silica. With a nonionic surfactant that forms vesicles and bilayers (polyoxyethylene alkyl ether C<sub>12</sub>E<sub>4</sub>), the effects of surface coverage are the same; however, the critical separation between particles is the thickness of two bilayers. Beyond full coverage, the surfactant forms a lamellar phase which excludes the particles.

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## 108.A6 COLLOIDAL STABILITY OF PHTHALOCYANINE PARTICLES IN A HYDROCARBON PHASE

Subhayu Basu<sup>1</sup>, Paul Jenkins<sup>1</sup>, John Ralston<sup>1</sup> and John C. Thomas<sup>2</sup>

<sup>1</sup>Ian Wark Research Institute

<sup>2</sup>School of Applied Physics, University of South Australia, The Levels, SA 5095, Australia.

Colloidal stability of nonaqueous dispersions of phthalocyanine particles has important implications in many technologically relevant systems such as printing inks, coatings, and paints. Although the importance of interfacial charge in controlling the suspension stability is well-documented, the mechanism governing the electrostatic charge generation in nonaqueous media is poorly understood. This work investigates the factors that control surface charging, and dispersion stability of phthalocyanine particles in a hydrocarbon phase in the presence of a particle charging agent (zirconium octanoate) and resins. Electrophoretic mobility, adsorption isotherm, and particles size distribution studies were conducted and the role of water, particle charging agent, and resins on electrical charging and colloidal stability is demonstrated. A particle charging mechanism is described to better understand the adsorption/desorption of mobile ions in solution onto the particle surface and correlated with the measured surface charge density data.



**109.A6****PARTICLE GELS AS STUDIED BY BROWNIAN DYNAMICS  
AND CONFOCAL SCANNING LASER MICROSCOPY****B.H. Bijsterbosch, M.T.A. Bos, J.H.J. van Opheusden and P. Walstra***Departments of Physical Chemistry, Agricultural Engineering and Physics and Food Science,  
Wageningen Agricultural University, The Netherlands*

Gels that are made up of particles have been far less extensively studied than macromolecular gels. However, investigating the formation process and the ensuing structure of particle gels not only meets with many scientific challenges, but is also of great practical interest, for instance with regard to food science.

In this paper we will present two different approaches. On the one hand, real gels have been prepared from perfluoro-alkoxy teflon particles and casein micelles (both solid materials). To avoid any effects of convection, the destabilization of the respective dispersions was accomplished by (slow) hydrolysis of glucono- $\beta$ -lactone in the homogeneous system. The structures that were obtained were assessed by means of Confocal Laser Scanning Microscopy (CSLM). To this purpose a number of improvements in the underlying image analysis technique had to be introduced. Some of these will be discussed. The ensuing structures were analyzed in terms of fractal dimensions, showing that one single value of the dimensionality does not suffice to characterize the gel throughout. Moreover, due to reorganization processes in the gels after they have been formed, both the dimensionality as well as the size of the building blocks appear to change in time.

In the second approach the formation of particle gels was simulated by means of Brownian Dynamics. Since this was a first approach, essentially to assess the feasibility of the method, relatively simple Lennard-Jones types of interaction potentials were used. Despite the difference between those and actual colloidal interactions and taking into account that computing capacity yet limits the particle number in this type of studies, some interesting results with regard to the dimensionality of the created gels were obtained.

**110.A6****MULTICOMPONENT LATEX FILMS - A COMPARATIVE STUDY  
OF CORE-SHELL LATICES AND LATEX BLENDS BY MICROSCOPIC METHODS****Albena Bojkova<sup>1</sup>, Stefan Krieger<sup>2</sup>, Alexander Du Chesne<sup>1</sup>**<sup>1</sup>*Max-Planck-Institut für Polymerforschung, PF 3148, 55021 Mainz, Germany*<sup>2</sup>*Hoechst-AG, 65926 Frankfurt am Main, Germany*

One disadvantage of latex films as compared to such cast from solution is that film formation proceeds only at temperatures above the minimum film forming temperature, which more or less depends on T<sub>g</sub>. On the other hand, desired film properties often require that T<sub>g</sub> is above ambient.

Blends of a high-T<sub>g</sub> and of a low-T<sub>g</sub> latex are promising to overcome this problem and have therefore been studied in detail. Core-shell lattices may have similar effects. In some cases "hard" films of a heterogeneous latex form even if dried at 80K below the T<sub>g</sub> of the latex shell. A change of morphology drastically alters the film forming behaviour.

In the present work we investigate film forming behaviour and film properties as a function of latex morphology. For this purpose, we have synthesised heterogeneous polyacrylate lattices with a high-T<sub>g</sub> core and a low-T<sub>g</sub> shell and vice versa of the same overall composition. For comparison, homogeneous lattices where synthesised of a mixture of the components of identical composition as well as of the pure components.

Structure and morphology of the lattices were investigated by DSC, AFM and electron microscopy. The coatings were investigated by TEM, optical and mechanical methods.

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**111.A6****LIGHT SCATTERING INVESTIGATIONS ON  
CRYSTALLIZING LYSOZYME SOLUTIONS****Yannis Georgalis, Patrick Umbach and Wolfram Saenger***Institut für Kristallographie Freie Universität Berlin, Takustr. 6, 14195 Berlin, Germany*

The system lysozyme-NaCl has been examined in the range of suboptimal and optimal crystallization conditions with dynamic and conventional static light scattering techniques. We have shown that nucleation at low volume fractions is nearly always accompanied by the appearance of fractal clusters. At higher volume fractions and lower temperatures the liquid-liquid region of the same system was examined by small-angle static light scattering and light microscopy. A first order analysis of the intensities revealed a Lifschitz-Allen-Cahn type of ripening. The behaviour of the system can be understood in this case as correlated ripening, leading to modulated phase type of microstructure. Interestingly, at high volume fractions all conditions examined did not promote the formation of fractals, as is usually the case at low lysozyme volume fractions. The described experiments raise the question whether droplets, forming at very early times and at low volume fractions via ripening, could transform to fractals if they do not attain a critical size that permits for sufficient ripening while attractive interactions prevail.

**112.A6****A FTIR STUDY OF DISSOLUTION AND PRECIPITATION  
OF SILICA IN BAYER PROCESS****Gong Wenqi***Department of Resources and Environmental Engineering, Wuhan University of Technology,  
Wuhan, P.R.China*

The reduction of caustic losses from the desilication of bauxites in alumina refineries requires the study of the dissolution in Bayer liquor of the silica containing minerals in bauxites and the precipitation of the desilication product (DSP). This involves the characterization of ultrafine materials such as complex bauxite or clay mixture of colloidal size. Fourier transform infrared (FTIR) spectroscopy was used for the study. A quantitative FTIR technique was established by comparison with chemical analysis and quantitative X-ray diffraction (XRD) analysis. By the quantitative FTIR analysis of bauxite during dissolution, the process of dissolution and precipitation of silica was found to occur in three stages. In the first stage, there was no precipitation of DSP. All the silica dissolved from kaolinite went into the solution. In the second stage, the silica concentration in solution attained a maximum and then dropped very quickly. The precipitation of DSP was the main cause of the reduction of the silica concentration in solution. In the third stage, the concentration of DSP reached a constant level. The dissolution and precipitation process gradually attained an equilibrium. The mechanism of silica dissolution and DSP precipitation was discussed on the basis of the FTIR quantitative analysis of kaolinite and DSP in bauxite.

**113.A6****CORE-SHELL LATICES AND LATEX BLENDS:  
INVESTIGATION OF THE FILM FORMATION BY (ELECTRO-) MECHANICAL  
AND DIELECTRIC SPECTROSCOPY****Gunnar Glaßer<sup>1</sup>, Stefan Krieger<sup>2</sup>, Katherina Landfester<sup>1#</sup>, Dieter Neher<sup>1</sup>**<sup>1</sup>*Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany*<sup>2</sup>*Hoechst AG, 65926 Frankfurt am Main, Germany*<sup>#</sup>*present address: Emulsion Polymers Institute, Lehigh University, Bethlehem, PA 18015, USA*

Thin films of core-shell latices and of corresponding blends of a high- $T_g$  and low  $T_g$  latex have been investigated by dielectric and (electro-) mechanical spectroscopy. Electromechanical experiments allow the non-destructive measurement of mechanical properties of even fragile materials in a temperature and frequency range accessible to dielectric spectroscopy.

Films prepared by spin coating from core-shell latices with the low  $T_g$  material forming the shell gave transparent and uniform films. Electromechanical experiments as function of temperature and frequency showed a continuous softening of the film but no significant indication of a particular glass transition.

Core-shell (poly(butylmethacrylate)-poly(methylmethacrylate)) latices with the high- $T_g$  polymer forming the shell form brittle and opaque films. Upon heating a sudden transformation to a dense and transparent film is observed, which is accompanied by sharp increase in mechanical modulus. This transformation takes place at a temperature  $T_i$ , between the  $T_g$ 's of the soft and hard phase and shifts towards higher temperatures with increasing thickness of the shell. After this transformation the electromechanical properties are identical to films prepared from the inverted structure (with the soft phase forming the shell). Dielectric spectroscopy experiments on these films before and after the transformation show that the relaxation properties of two phases are maintained.

The densified material can thus be treated as a composite of a hard and a soft phase, with the macroscopic mechanical properties mainly determined by the volume fraction of the two components. These observations are compared to the behavior of latex blends of similar compositions of the soft and hard phase.

## 114.A6      LABORATORY STUDIES OF CRYSTALLIZING THE BOUNDED WATER IN SAND SOIL

Ilyin, V.A.<sup>1</sup>, Smorodin, V.Ye.<sup>2,3</sup>, Bakhtina, E. Yu.<sup>1</sup>

<sup>1</sup>Phys. Dept., Moscow Pedagogic State University, Malaya Pirogovskaya, 29, Moscow 119435, Russia

<sup>2</sup>Chem. Dept., Moscow State University, Moscow 119899, Russia;

<sup>3</sup>Inst. Chem. Biol. Techn., R. Quinta Grande, Apt. 127, 11-2780 Oeiras, Portugal

Peculiarities of the bounded water at wide temperature range (from +30°C to -25°C) in sand soils are investigated studying its dielectric permittivity in the ultrahigh frequency range ( $l=15$  mm). This range is the most optimal for studying the bounded water in view of smaller value of the relaxation wavelength of the last than in a case of free water.

The most interesting dependences of the real part of the permittivity on temperature correspond a middle value of the sand humidity:  $W=9-14\%$ . It is worth to underline that at some negative temperature these dependences have minimum. An analysis of such unusual dependences shows that its cause is the bounded water crystallization. Interpreting these data we have suggested that the frozen boundary water layers have segnetoelectric properties. Possible mechanisms of the phenomena and effects of the sand particle heterogeneity are experimentally studied, modelled and theoretically interpreted.

Our results are important for the space remote sensing of the water content and stage in the planetary soil layer.

## 115.A6      PORE TEXTURES AND BULK PROPERTIES OF BINARY BIVALENT AND TRIVALENT METAL HYDROXIDES PREPARED DURING SUCCESSIVE CATIONIC PRECIPITATION

T.F. Kouznetsova\*, G.S. Lemeshonok, S.I. Yeremenko

*Institute of General and Inorganic Chemistry, Byelorussian Academy of Sciences, Minsk, Belarus*

The surface area and porosity of several successively precipitated binary hydroxides ( $Ni^{2+}/Cr^{3+}$ ,  $Co^{2+}/Cr^{3+}$ ,  $Zn^{2+}/Cr^{3+}$ ) with respect to the  $Me^{2+}/Me^{3+}$  ratio in the initial solution, gel thermal activation conditions, and sodium metavanadate treatment of hydrogels have been determined. The results are correlated with X-ray powder analysis.

Sodium hydroxide neutralization curves for mixed metal chloride solutions were obtained. Successive precipitation of binary systems is shown to form together with an amorphous phase a layered binary structure, whose interlayer space is fixed by sodium metavanadate at low  $Me^{2+}/Me^{3+}$  ratios. The

presence of a layered binary structure, preventing bivalent metal hydroxide from dehydration and crystallization, changes the adsorption and structural properties of porous materials obtained upon thermal treatment of gels.

Conclusions are presented on the effect of anion exchange in interlayer space of binary hydroxides and on the permeability of it to  $\text{CCl}_4$  and  $\text{H}_2\text{O}$  vapour molecules.

## 116.A6 ACTION MECHANISM OF SURFACTANTS IN THE PROCESSES OF GLASS CANVAS MANUFACTURING

Krut' V.V.<sup>1</sup>, Zharov A.I.<sup>2</sup>, Novikova E.N.<sup>2</sup>

<sup>1</sup>NPAO "SintezPAV" Russia

<sup>2</sup>Joint Stock Company "Sudogodskoe Steklovolokno"

The surfactants used in the manufacturing processes of glass canvas based on aqueous glass dispersions act as oiling agents, dispersants and activators for binding additives. The paper deals with the action mechanism of cationic, ampholytic and anionic surfactants and their mixtures as modifiers of glass fibre surfaces in the steps of oiling, dispersing and binding. Discussed are also promising applications of glass canvas and glass fibres in the processes of manufacturing filled polymeric materials. The effect of surfactant structures on the dispersive power of glass fibres in water as well as on physico-chemical characteristics of glass canvas and its compatibility with polymeric materials was studied. It has been established that the action of surfactants on a glass fibre surface is due to the peculiarity of interaction of the formed surfactant structures with the glass surface elements. The formation of complex surface compounds during chemisorption is a basis for the development of surface structures, especially in the oiling step, which determine subsequent dispersion and ant cohesion properties of the dispersion particles. These structures are also active centres in glass fibre-polymer interactions. This mechanism opens new prospects for the creation of absolutely new technologies saving energy and material consumption due to the elimination of the chemical surface modification of polymeric materials and the decrease in the number of components used in oiling agents, dispersants and binders, e.g. from 5-12 down to 2-3 components.

## 117.A6 CHARACTERIZATION OF CATIONIZED STARCH FROM GENETICALLY MODIFIED POTATO USING LIGHT SCATTERING TECHNIQUES

Anders Larsson<sup>1</sup> and R.H. Ottewill<sup>2</sup>

<sup>1</sup>Department of Physical Chemistry, Gothenburg University, Gothenburg, Sweden

<sup>2</sup>Department of Physical and Theoretical Chemistry, University of Bristol, Bristol, United Kingdom

Starch is stored in plants in a granular form. The size range of these granules is 10-150  $\mu\text{m}$ . The major components in the granules are the linear "low" molecular weight amylose ( $10^5$ - $10^6$  g/mole) and high molecular weight branched molecule amylopectin ( $10^7$ - $10^8$  g/mole). Ordinary potato starch consists of 20 % amylose and 80 % amylopectin. Recently a strain of potato producing only amylopectin has been produced by genetic modification. Potato starch of this kind has been obtained from Lyckeby Stärkelsen, Kristianstad, Sweden. The granules from the genetically modified potato was cationized with a quaternary amine and the degree of cationisation became 5.2 %.

The dimensional properties of the molecularly dispersed starch has been analysed using time averaged light scattering and dynamic light scattering. The molecular weight is approximately  $10^8$  g/mole and the hydrodynamic radius 100 nm.

**118.A6****DYNAMICS OF ROUSE NETWORKS****P. Licinio and A.V. Teixeira***Dep. de Física - Universidade Federal de Minas Gerais - Belo Horizonte - Brasil*

Dynamic phenomena in polymer gels have often been considered from the point of view of the anomalous diffusion of a particle in a fractal percolation substrate. In this work we call attention for the self dynamics of a gel network. We study the self diffusion of the thermally driven structure fluctuations. Internal dynamics of swollen polymer arrays were investigated with Brownian dynamic techniques applied to regular Rouse networks. In all cases local or self diffusion decayed as a power law with a power proportional to the given topological (graph) dimension. This behavior allows for the classification of three dynamic regimes: sub-critical topologies accommodate power law anomalous diffusion; logarithmic anomalous diffusion occurs within the critical dimension 2D for surface arrays; and upper-critical topologies, as those prevailing in gels, siege bounded anomalous diffusion. We also give experimental evidence that PMMA gel dynamics follows closely the Rouse model, which can be accounted for by hydrodynamic screening effects.

**119.A6****AUC-STUDIES OF STRUCTURE, SWELLING AND DISSOLVING BEHAVIOUR OF HIGHLY CARBOXYLATED LATEX PARTICLES****W. Mächtle, G. Ley, H. Wiese***Polymer Research Laboratory, BASF Aktiengesellschaft, D-67056 Ludwigshafen/Rhein, Germany*

There is a hypothesis of Snuparek et al., Collect. Czech, Chem. Commun. 58 (1993) 2451 that highly carboxylated latex particles are composed of "precursor" particles. These primary particles originate from aggregation process during the emulsion polymerization at low pH by the mechanism of homogeneous nucleation. At high pH these latex particles should be disintegrated into the precursor particles. We checked this hypothesis using 85EA/15MAS-, 85EMA/15MAS- and 85n-BA/15MAS-copolymer latices. These types of latices are of interest in applications such as thickeners, cobinders and ion exchange dispersions. In a first step particle size distribution (PSD) and the particle density in the aqueous medium at low pH were measured to characterize the original latices using the analytical ultracentrifuge (AUC). Then we transferred the latices into an organic medium by 1:100 dilution with tetrahydrofuran (THF), which is miscible with water and at the same time a good solvent for the emulsion polymer. We then measured molar mass distribution and microgel content. In the EMA/MAS- and the n-BMA/MAS-System we see no microgel, but only dissolved macromolecules. In Snuparek's EA/MAS-System, apart from dissolved macromolecules, about 10 wt.% of microgel particles are found. We will discuss whether these microgels can be regarded as Snuparek's precursor particles. By variation of  $2 < \text{pH} < 12$  we studied the swelling and dissolving behaviour of our various copolymer latices. Depending on the molar mass  $M$  of these latices either no dissolution and only little swelling or else complete dissolution takes place at around  $\text{pH} = 8 - 9$ . It seems there is a critical molar mass of entanglement which governs dissolution.

**120.A6****BEHAVIOR OF NEW LIQUID CRYSTALLINE COMPOSITIONS WITH AROMATIC PRINCIPLE AS NON-MESOMORPHIC COMPONENT****Manko A.A., Volchkova I.L., Matveenko V.N.***Department of Chemistry, Moscow State University, 119899 Moscow, Russia*

Properties of liquid crystalline compositions are of great interest because of their practical applications (e.g. based on the increasing of the temperature interval of mesophase existence) as well as their theoretical significance for the further understanding of mesophase nature. Physical investigation of such systems based on the principle of state diagrams of condensed matter.

Research of phase transitions and some surface properties in the compositions of two nematic LC's (5-cyan-biphenyl and p-oxybenzoic acid) with non-traditional mesomorphic component, (p-hydroxyphenyl) - methylethylketone, known as trade aromatic principle, "raspberry ketone" was carried out by means of DSC and Polytemperature Polar Microscopy in wide temperature interval (0-80 °C) with contains of aromatic principle varied from 10 to 90 mole per cents.

Phase diagrams obtained by us have narrow areas of components coexistence in nematic and isotropic phases, eutectic points that we believe appeared due to complex formation between components.

These objects are suggested for obtaining the effect of "controlling smell" in case of convenient LC concentrations and temperature range as the base idea for new high technology.

## 121.A6

### ENCAPSULATION OF MAGNETIC FLUIDS

C. Menager, S. Neveu, R. Letellier, V. Cabuil

*Laboratoire Physicochimie Inorganique, Université Pierre et Marie Curie - CNRS 4, place Jussieu,  
75252 Paris Cedex 05, France.*

Superparamagnetic suspensions, usually called ferrofluids, are colloidal solutions of ferromagnetic nanoparticles. Their applications are numerous in the field of the storage of information or for medical imaging. Particles are ferric oxide grains and may be coated either by surface charges or by surfactants: in the first case they will be dispersible in water; in the second case, they will be dispersible in organic solvents.

For many applications, magnetic fluids may not be incorporated in the medium as they are, and encapsulation processes have to be used. We shall describe here the encapsulation of aqueous ferrofluid into rigid capsules and into liposomes.

The methods we used are "multiple emulsion" processes. To synthesize magnetic capsules, an aqueous magnetic field is emulsified in oil with a polymerizable surfactant. Once the interface is polymerized; capsules are covered by another surfactant in order to be dispersed in water. To synthesize magnetic liposomes, an aqueous ferrofluid is emulsified in a low boiling point oil with a phospholipid. The emulsion is itself dispersed in water and oil is evaporated in order to get the phospholipidic bilayer. The microscopic objects we obtain align in a magnetic field gradient. Anisotropic magnetic objects have also been synthesized mixing phospholipidic tubules with an aqueous magnetic fluid. All these microscopic objects are well suited for technological or biomedical applications.

## 122.A6

### THE ADSORPTION METHODS FOR THE ORGANIC SUSPENSION SEDIMENTATION STABILITY INCREASE

S.S. Mikhailova T.P. Kolesnikova

*Institute of Physical Chemistry, Russian Academy of Science, Moscow, Russia*

The production of the sedimentation stable organic suspensions with multicomponent disperse phase is a central problem of the interface and colloid science. In the present paper we present the results of investigations of the adsorption stabilization with respect to the sedimentation of organic suspensions containing organic solvents or the solutions of epoxide esters as a dispersion medium and mixture of fine and coarse mineral and metal fillers (aluminium powders with different dispersity; highly dispersed mineral powders  $S \sim 300 \text{ m}^2/\text{g}$  coarse powders - the aluminium corundum particles of size  $\sim 800 \mu\text{m}$ ; the aluminium slime particles of size  $\sim 1250 \mu\text{m}$ ) as a disperse phase. It is known, that the interaction of disperse phase with dispersion medium determines the sedimentation stability and physico-mechanical properties of organic suspensions. This interaction reveals itself in the wetting, adsorption, structurization and etc. In this connection, the adsorption of low and high molecular surface active modifiers (surfactants and polymers) on the fillers was studied. The data obtained were compared with the results of investigations of the influence of adsorption modification carried out in different ways on the processes of sedimentation, structurization and packing density of particles in sediments. Our investigations were allowed to determine the optimum conditions for the adsorption modification and to carry out their classification according to efficiency. In the

polymer suspensions with coarse disperse filler and in the suspensions of organic solvents containing fine metal fillers the essential increase of sedimentation stability of suspensions can be achieved by modification of solid disperse phase components with single low or high molecular surfactants, or with one polymer modifier, or by sequential modification with two surfactants. In the suspensions with organic solvent as a dispersion medium and coarse or metal fillers of different dispersity, the most effective way to increase the sedimentation stability is the sequential modification of surface fillers with combinations of surfactants and polymers, or with two polymers. In this case, the modification of fillers with single surfactant is an ineffective method. The necessary condition for the increase of the suspension sedimentation stability is the formation of chemisorption layers lyophilizing the particle surface with respect to dispersion medium.

### 123.A6 PREPARATION AND PROPERTIES OF ORGANIC DISPERSIONS OF MONODISPERSE SILICA RECEPTOR COLLOIDS GRAFTED WITH CALIXARENE-DERIVATIVES OR ALKYL CHAINS

A.M. Nechifor<sup>1,4</sup>, A.P. Philipse<sup>2</sup>, F.de Jong<sup>2</sup>, J.P.M. van Duynhoven<sup>3</sup>, R.J.M. Egberink<sup>1</sup> and  
D.N. Reinhoudt<sup>1</sup>

<sup>1</sup>*Department of Organic Chemistry, University of Twente Enschede, The Netherlands*

<sup>2</sup>*Van't Hoff Laboratory for Physical and Colloid Chemistry, Debye Research Institute, Utrecht,  
University Utrecht, The Netherlands*

<sup>3</sup>*Department of Chemical Analysis, University of Twente, Enschede, The Netherlands*

<sup>4</sup>*On leave from: Research Center for Macromolecular Materials and Membranes, Bucharest, Romania*

We introduce cation-selective receptor colloids consisting of a monodisperse inorganic silica core grafted with an organic layer containing calixarene receptor molecules. The surface layer is designed to provide chemical selectivity (towards Cs<sup>+</sup>) as well as colloidal stability in organic solvents of interest in which silica spheres otherwise may flocculate.

Grafting procedures for commercial and laboratory-made silica dispersions are investigated for 25,27-bis[1-(11-hydroxyundecyl)oxy]calix[4]arene-crown-6 (designed and synthesized for this purpose), octadecyl alcohol, and mixtures ("co-grafting") of both compounds. Special attention is given to the nature of the solvent, which markedly influences grafting densities and colloidal stability during and after grafting procedures.

NMR elemental analysis, and light scattering are used to characterize a variety of carefully purified, grafted silica dispersions and to demonstrate, among other things, the presence of calixarene groups on the silica spheres. Preliminary complexation experiments with cesium chloride are reported. NMR and electrophoresis indicate that calixarene-silica colloids indeed are receptors for cesium cations.

### 124.A6 GELL PARTICLES SOLUBILITY IN REGARD TO MAGNETIC TREATMENT OF CELLULOSE COLLOIDAL SOLUTIONS

Mitko Nenkov

*Harmoni Priv. Co. Svishtov - Bulgaria*

Homogenization level of cellulose colloidal solutions for fiber forming is crucial for fiber even forming process. Viscose for fibrillation contains unsolved gel particles of semi-xanthation cellulose resin, mineral salts etc. They handicapped forming of the fibers and rayon and reduce the final products quality.

The present work is purposed to search possibilities for homogenization of dissolved cellulose xantogenat through magnetic field treatment. The number of gel particles was measured in coloured viscose drop by microscopic method. The number of gel particles was considered according the third group of Hembray classification.

The specific conditions of the experiment include magnetic field intensity, linear flow velocity flow orientation, type of magnetic poles, viscose was thermostated. The samples were taken from the Rayon plant at Svilozha Co - Svishtov. The measurement was conducted in two aspects - immediately after magnetic treatment and after 1.5 hours. In both cases the result is considerable: immediately after the viscose

treatment the reducing of gel particles number is 23.1 % and 1.5 hour later it is 18.7 %. The level of homogenization of cellulose solutions is increased as immediately after magnetic treatment so 1.5 hour later. Even of the fact that there is a real possibility of secondary gel formation during the course of time, it was noticed that the average number of gel particles in the treated samples remains constant.

## 125.A6 COLLOID PARTICLE AGGREGATION IN CURING POLYMER FILMS

V.I. Roldughin and V.V. Vysotsky

*Institute of Physical Chemistry RAS, Moscow, Russia*

Computer simulations and experiments with model systems have shown, that during aggregation of colloid dispersions the fractal clusters or geometrical objects, having a self-similar structure in various space scales will be usually formed. All conducted earlier numerical and model experiments concerned to systems, the properties of which do not change during aggregation. At the same time, there is a rather wide class of colloid object, which parameters can be changed during formation of the aggregate structure. The colloid dispersions based on thermosetting polymers are of this class. In such systems "viscosity" of a solution is changed with time, that introduces an essentially new element in dynamics of colloid systems. Varying regimes of the curing, we can change the moment of system hardening and observe the process of aggregate formation without disturbing its dynamics.

In experiments, the structural characteristics of aggregates of carbonyl nickel particles (8 microns in diameter), formed in thermosetting polymer (epoxy resin) films were studied at various regimes of curing, and influence modification of particle surface with stearic acid on aggregate structure was investigated. Experiments have shown, that the fractal dimensions of aggregates of nonmodified and modified particles have appeared to be close to value corresponding to the diffusion controlled aggregation, despite the change of viscosity of colloid dispersions during curing and difference of aggregation regime from that realized in computer simulation and model experiments. The change of viscosity of a dispersion during the curing effects only on the average size of aggregates: it increases with the temperature of curing. The modification of particles results not only in quantitative, but also in qualitative change of distribution of aggregate sizes: while the aggregates of nonmodified particles are characterized by lognormal distribution, the aggregates of modified particles have the bimodal size distribution. A probable explanation of a nature of the bimodal distribution consists in follows. Modification of particles results in aggravation of their compatibility with polymer matrix, and they are pushed out from the film bulk. As a result two aggregation processes, surface and bulk ones, take place in the system. Thus, two groups of aggregates are formed with their average sizes providing the bimodality of the global size distribution.

## 126.A6 FACTORS AFFECTING THE SWELLING OF POLY(NIPAM) MICROGEL PARTICLES - FUNDAMENTAL AND COMMERCIAL IMPLICATIONS

Brian R. Saunders, Helen M. Crowther, Gayle E. Morris and Brian Vincent

*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 ITS, U.K.*

A microgel particle is a crosslinked latex particle which is swollen by a good solvent. Particle swelling is intrinsically related to the nature of the interaction between the polymer and continuous phase. Microgel particles based on poly(NIPAM) (NIPAM = N - isopropylacrylamide) are particularly interesting since the parent homopolymer undergoes a coil-to-globule transition when the solution temperature increases above 32 °C. This phenomenon causes deswelling of poly (NIPAM) microgel particles and is examined herein. PCS (photon correlation spectroscopy) and SANS (small-angle neutron scattering) are employed in a complementary manner to study the environmentally-induced deswelling of poly(NIPAM) particles. Further, we show that particle deswelling may be induced at room temperature by addition of alkanols or excluded free polymer (i.e., non-adsorbing free polymer) to the continuous phase. (The extents of particle deswelling observed using these additives are similar to those achieved by heating the pure microgel in water above 32 °C.) Particle deswelling in the presence of added alkanol or free polymer arises from cononsolvency and osmotic deswelling effects, respectively.



Emulsion copolymerization of NIPAM with acrylic acid yields a microgel whose diameter is sensitive to both pH and temperature. These particles exhibit the ability to adsorb heavy metal ions from solution in a reversible manner and a mechanism for adsorption is proposed. The latter property has potential application in water purification. The data presented are used to propose a structural model for the monomer/charge distribution throughout poly(NIPAM) microgel particles.

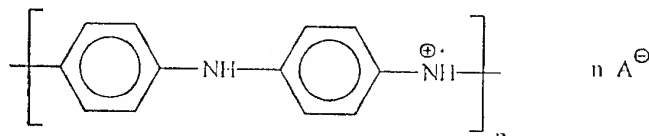
## 127.A6 DISPERSIONS OF ELECTRICALLY CONDUCTING POLYANILINE

Jaroslav Stejskal<sup>1</sup>, Andrea Riede<sup>2</sup> and Martin Helmstedt<sup>2</sup>

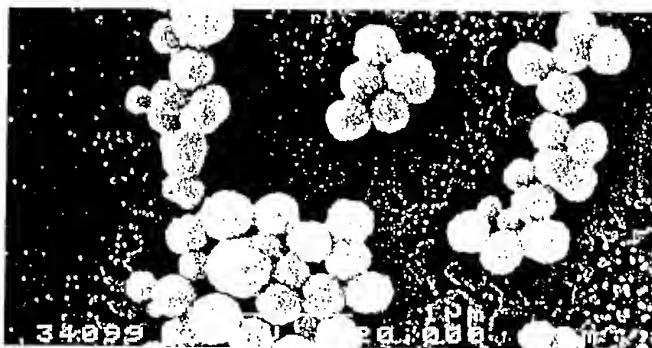
<sup>1</sup>*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic 16206, Prague 6, Czech Republic*

<sup>2</sup>*Faculty of Physics and Geosciences, University of Leipzig, 04103 Leipzig, Germany*

Polyaniline is one of the most interesting electrically conducting polymers<sup>1</sup>. It can exist in a variety of protonation and oxidation states<sup>2</sup> that differ in optical and electrical properties. Green electrically-conducting protonated emeraldine form of polyaniline is the most important one:



When aniline is oxidized with ammonium peroxydisulfate in the presence of colloidal silica, composite polyaniline-silica particles of submicrometer size are obtained<sup>3</sup>.



Dynamic light scattering was used to monitor the course of dispersion polymerization of aniline. The increase of hydrodynamic radius of particles was observed as polyaniline had been produced. The rate of aniline polymerization was found to increase with increasing temperature in the range 0-50°C. At low temperature, well-defined particles are formed while above 30 °C the colloidal stability of resulting systems is limited.

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3. Stejskal J., Kratochvil P., Armes S.P., Lascelles S.F., Riede A., Helmstedt M., Prokes J. and Krivka I. *Macromolecules* 29, 6814 (1996).

## 128.A6 INCLUSION COMPLEX OF $\beta$ -CYCLODEXTRENE AND ITS OXY-PROPYL-DERIVATE WITH Cr(III) SALTS

Volchkova I.L., Putilin A.F., Matveenko V.N.

*Department of Chemistry, Moscow State University, 119899 Moscow, Russia*

Studies of "host-guest" complex formation attract more and more attention of the experts in different fields of science and technology in the last years. One of the most interesting area of this field is complexation of inorganic ions with man-made organic lizards, such as crown-ethers and cyclodexrenes (CD) with the latter group playing the host-role.

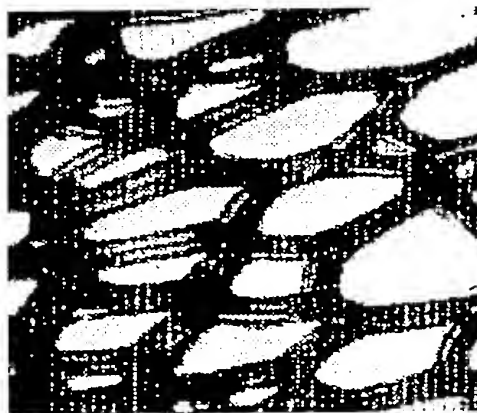
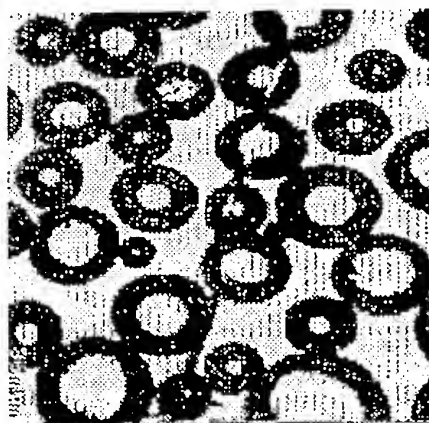
A number of complexes of CD's and their derivatives with hydrophobic organic compounds have been already recommended as medical drugs. That allows wide usage of CD as microcapsulating agent, as ages, and as transporting agents for lupophylic vitamins and oxidants in foods.

In this work the studies of Cr(III) nitrate reactions with  $\beta$ -CD and its oxypropyl-analog ( $\beta$ -CDOP) in water solutions and in solid state are presented. The experimental data indicates, that crystallization processes of  $\beta$ -CD and  $\beta$ -CDOP in presence of Cr(III) nitrate are different from one another. In case of  $\beta$ -CDOP crystallization process was found to be Cr(III) concentration-dependent.

The analysis at this stage was done by microcalorimetry and X-ray analysis white rectangular crystals were obtained from the solution of  $\beta$ -CD, and  $\text{Cr}(\text{NO}_3)_3$  mixture. The X-ray structure and DSC-thermograms indicate this product to be  $\beta$ -CD.

The microphotographs of the compounds obtained from  $\beta$ -CDOP solutions with different Cr(III) concentrations are depicted in Figure. In 2:1 molar ratio of Cr(III) and CDOP in solution, the formation of solid amorphous structure was observed.

In the solid state, the mixtures of Cr(III) nitrate and  $\beta$ -CD and its derivatives behave in the same way on solutions. Complexation formation was detected by the powder color change the absence of melting peak of  $\text{Cr}(\text{NO}_3)_3$  and absence of dehydration peak of  $\beta$ -CD on the DSC curve.



## 129.A6 FLOCCULATION OF SILICA PARTICLES AND CATIONIC POLYMERS STUDIED WITH AN ELECTROACOUSTIC METHOD

Charlotte Walldal and Staffan Wall

*Physical Chemistry, University of Göteborg, Sweden*

The flocculation between silicic acid and two cationic polymers with different molecular weight was studied with a Matec ESA-8000 apparatus. The ESA apparatus measures the dynamic mobility of colloidal particles in suspensions. The size of the flocs was measured with a laser diffraction instrument (Malvern 2600).

The silica sol used was monodisperse with spherical particles with a hydrodynamic diameter of 140 nm. A cationic polyacrylamide was used with 10% of the acrylamide groups exchanged for trimethylaminoethylacrylatechloride (a charge of 1.25 meq/g). The molecular weight was  $1 \times 10^6$  g/mol. The other polymer was a polyamine with a molecular weight of  $50 \times 10^3$  -  $200 \times 10^3$  g/mol and a charge of 6 meq/g at pH 7. The experiments were performed at 10 mM NaCl and at pH 7.

The adsorption of polyelectrolytes neutralised the particle charges, flocs were formed and the magnitude of the dynamic mobility was reduced. When a certain amount of polyelectrolytes was added a charge reversal occurred and the flocs became positively charged.

It was shown that it is possible to perform reproducible measurements of the dynamic mobility of the flocs with the ESA technique. The particles were flocculated by each of the polymers separately or by a mixture of them. Two different ways of mixing polymers and particles were employed. On one hand the polymers were poured into the particle dispersion and on the other hand polymers and particles were added at the same time into the ESA apparatus.

The same amount of polymer charges from both polymers was needed to obtain a charge reversal of the flocs. A surplus of polymer charges compared to silica charges was needed to obtain a charge reversal.

When the particles were flocculated with the same amount of polymer charges, but with mixtures of different proportions of polyacrylamide and polyamine, the obtained dynamic mobility differed.

In one part of the investigation, polyamine was added 30 s before polyacrylamide to the particles.

The contribution to the ESA-signal from non adsorbed polymers was negligible compared to the ESA-signal from the particles.

## 130.A6 QUANTITATIVE DESCRIPTION OF MASS INHOMOGENEITY IN CONTROLLED AGGREGATION AND FRAGMENTATION OF COLLOIDS

Josiane Widmaier and Emile Pefferkorn  
*Institut Charles Sadron, Strasbourg, France*

The destabilisation of hydrated colloidal latex particles in aqueous electrolyte solution was found to produce aggregates with unusual mass frequencies. The analysis of the mass frequency curves allowed to determine the presence of at least three aggregate populations growing at different rates. For each population, we determined the variation with time of the number and weight average masses and their relative concentration inside the suspension. The fragmentation of large aggregates was induced by decreasing the ionic strength of the suspending medium at constant pH. Instantaneous fragmentation of the aggregates and subsequent slow break-up of the fragments were investigated by determining the variation with time of the suspension characteristics. The aggregation mechanism was found to belong to the class of reversible diffusion-limited processes. The formations of three aggregate populations was partly attributed to the unusually low energy of the attractive forces engaged in the process. Actually, since electrical forces were of short range in the concentrated electrolyte medium, hydration forces were considered to oppose the attractive forces. This situation led us to assume that the structure dependent reversibility of aggregate formation also contributed to the formation of three populations. Typical structures were designed for each population aggregates whose interparticle bonds are only linear were attributed to population 1, aggregates with double or triple interparticle contact points were attributed to population 2 and aggregates with multiple contact points or ring forming links were attributed to population 3. Combination of the internal stability and collision efficiency, both dependent on the aggregate structure, led to the well differentiated growth of the three populations. Preservation of these populations during fragmentation was attributed to their different internal stabilities. The structure of large aggregates appeared to be very complex since their fragments may be ranked among different populations. The absence of self-similarity in the mass frequencies determined at different times led us to envisage that the aggregation process should escape the analysis on the basis of the usual mean field approach of Smoluchowski.

## 131.A7

ON THE MEASUREMENT OF KINEMATIC VISCOSITY  
OF AEROSOL SYSTEMS

K. Damov, A. Antonov

*South-West University "Neofit Rilsky", 66 Ivan Mihailov Str. 2700, Blagoevgrad, Bulgaria*

The aerosol systems with an own volume have properties analogical to those of liquids [1,2] and give a possibility for measurement of the kinematic viscosity of the aerosol due to the existence of "hydrostatic pressure" in it. Method for such kind of measurements has been described in [3,4]. It is based on the supposition that the aerosol flows out from a vertical vessel via a horizontal tube near the bottom according to the Poisson's law. In this paper the method is generalized in case of nonhomogeneous aerosol with a kinematic viscosity which depends on the time and height above the bottom of the vessel

For the kinematic viscosity, we obtain the following expression:

$$\nu(H, \tau) = cHt,$$

where  $t$  is the time for decreasing of the free aerosol boundary with a distance step of  $\Delta H$  around the height  $H$ ;  $c$  is the instrumental constant.

The measurements are carried out at various delay times (i.e. the times of evolution of aerosol from its formation till the moment of measurement). The dates for existence of a phase transition "liquid-gas" are obtained at long times of evolution.

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## 132.B1 AN AUGER, LOW ELECTRON ENERGY LOSS SPECTROSCOPY AND SDM STUDY OF LIQUID AND SOLID In, Sn, Bi AND In-Bi, Sn-Bi ALLOYS

Achkhotov O.G., Zdravomislov M.V.

*Kabardino-Balkarian State University, ul. Tchernishevskogo 173, Nalchik, KBR, Russia.*

The liquid and solid indium, tin, bismuth and alloys In-Bi, Sn-Bi from 300 to 500K have been investigated using Auger electron spectroscopy (AES), low electron energy loss spectroscopy (LEELS) sessile drop method (SDM).

The spectrometer consisted cylindrical mirror analyzer and a coaxial electron gun with a 2,5mA, 50-500 eV beam (spot size 0,1 mm) could be generated for LEELS and a 3 mA, 3 keV could be generated for AES. The energy width of the elastic peak was 0.9eV at 100 eV, which was important for our requirement to resolve peak of plasmons. All LEELS and AES spectra were made in first derivative mode with a 0,2 and 1 eV modulation amplitude for LEELS and AES respectively.

An Ar ion beam with an energy of 0.6 keV was used for clean samples. Samples were ion etched until AES spectra was determined surface to be atomically clean. In case of indium, as was show early on the surface was also sulphur, which back in bulk by melting of sample.

Because of the orientation of the ion beam, approximaly one-third of the surface of sample could not be ion etched. After melting conthentration of contaminations became increased due to the migration of the unsputtered path of surface. The ion gun was again turned on the molten surface would remain free of contamination.

The surface compositions, surface tension and loss spectra of seven alloys in the In-Bi and Sn-Bi systems have been obtained as a function of temperature in both solid and liquid states. Bismuth has been found to be the segregating component in all cases. These results are interpreted in the light of current segregation theories.

Reported an evaluation of the surface tension of liquid In, Sn, Bi, and In-Bi, Sn-Bi alloys. Our data of the surface tension for investigated alloys are more higher then those early. After cleaning procedure the surface tension of pure liquid In, Sn, Bi can be represented by equations  $\sigma_{In}=701 - 0,045 \cdot (t - t_m)$ ,  $\sigma_{Sn} = 645 - 0,1 (t - t_m)$ ,  $\sigma_{Bi} = 474 - 0,15(t - t_m)$  respectively.

## 133.B1 THERMODYNAMICS OF 2-D NEW-PHASE FORMATION ON LIQUID-GAS INTERFACE

M. Avramov, B. Toshev and B. Radoev

*University of Sofia, Department of Physical Chemistry, 1126 Sofia, Bulgaria*

The effect of electric charge on the formation of flat spots of surfactant on the gas-liquid interface is considered. The process, well registered experimentally by the methods of Brewster Angle Microscopy (BAM), might be described as a 2-D nucleation. Two cases are analyzed: (i) closed system of insoluble surfactants - the equilibrium conditions are found when the variation of the Helmholtz free energy of the system is zero; (ii) open system of soluble surfactants at constant chemical potentials - then a characteristic function is the  $\Omega$ -potential. The stability conditions in both cases are also established. Similarly to the barrier-less condensation upon electrically charged free droplets, stable spots in the interface could exist. It seems that the size of those spots is of the order of the size of the spots observed by the method of BAM.

## 134.B1 A GENERALIZED SCALE FOR FREE ENERGY OF ADSORPTION FROM GIBBS ADSORPTION EQUATION

D.K. Chattoraj

*Department of Food Technology and Biochemical Engineering, Jadavpur university,  
Calcutta-700 032, India*

From boundary tension, analytical and isopiestic vapor pressure techniques, substantial amount of experimental data on extent of adsorption ( $\Gamma_2^1$ ) of solutes (surfactants, fatty acids, inorganic salts, sucrose and urea) at liquid as well as solid surfaces suspended in aqueous media at different bulk solute activity ( $a_2$ ) are available for calculation of free energy of adsorption. Values of  $\Gamma_2^1$  increases with increase of solute activity so that its hypothetical value at unit activity in each case has been calculated. Using all these experimental and hypothetical values in the integrated forms of the Gibbs adsorption equations for multi component solutions, the standard free energy change  $\Delta G^0$  in KJ/meter<sup>2</sup> unit have been evaluated for different systems for the change of bulk solute activity from zero to unity in the rational scale. For surfactants  $\Delta G^0$  is negative since  $\Gamma_2^1$  is positive whereas for inorganic salts, sucrose and urea,  $\Delta G^0$  is positive since  $\Gamma_2^1$  is negative. All values of  $\Delta G^0$ , positive or negative refer to unit solute activity in this generalized scale of free energy of adsorption and hence order of their values expresses relative measure of affinities of solutes and solvents for different types of liquid and solid surfaces. Also using the Gibbs adsorption in an alternative form, the excess free energies of hydration of different surfaces in a different thermodynamic scale may be evaluated.

## 135.B1 THE EFFECT OF OIL CHAIN LENGTH ON INTERFACIAL PHASE TRANSITION IN THREE-COMPONENT WATER + OIL + NONIONIC SURFACTANT SYSTEMS

Li-Jen Chen, W.-J. Yan, and F.-S. Shau

*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 106, Republic of China*

In a three-phase  $\alpha$ ,  $\beta$  and  $\gamma$  equilibrium system, the middle  $\beta$  phase can obviously either wet or not wet the interface between the upper  $\alpha$  and the lower  $\gamma$  phase. At different thermodynamic conditions, the  $\beta$  phase exhibits a transition from a wetting regime to a nonwetting regime, or vice versa. This phenomenon is called a  $\beta$  phase wetting transition. While for some three-phase coexisting systems, due to the effect of interfacial tensions, a small amount of  $\gamma$  phase forms an intruding layer (wetting behavior) or suspending beads (nonwetting behavior) between the  $\alpha$  and the  $\beta$  phase. The transition from an intruding layer to suspending beads, or vice versa, at the  $\alpha\beta$  interface is called a  $\gamma$  phase wetting transition.

In the three-liquid-phase coexisting region of the system water + n-tetradecane + diethylene glycol monoethyl ether ( $C_6E_2$ ), the  $\beta$  phase wetting transition occurs as the temperature is raised toward its upper critical consolute temperature. While the temperature is decreased toward its lower critical consolute temperature, the  $\gamma$  phase wetting transition is observed. (J. Chem. Phys. 98, 4830, 1993).

In this study, the effect of oil chain length on the wetting transition in the system water +  $C_6E_2$  + oil (n-tetradecane, n-dodecane and n-decane) is investigated by direct interfacial tension measurements. The image digitization technique is applied to pendant drop method in the interfacial tension measurement. The  $\beta$  phase wetting transition is observed in all three systems while the system is driven to its upper critical point. On the other hand, the  $\gamma$  phase wetting transition also appears in all three systems when the system is approaching its lower critical point. Decrease of oil chain length in the system water +  $C_6E_2$  + oil would make the three-phase body shrink and lead the system to approach a tricritical point, which is also discussed in this study.

## 136.B1

ALTERNATIVE ARRANGEMENTS FOR MEASURING  
LINE TENSION ON NON-FLUID SUBSTRATES

J. Gaydos

*Department of Mechanical and Aerospace Engineering, Carleton University, Ottawa, Canada*

Virtually all experimental procedures for measuring the line tension employ axisymmetric arrangements (e.g. sessile drop on solid substrate, liquid lens, etc.). From the viewpoint of the modified phase rule [1] we shall discuss a number of inherent limitations that exist when these axisymmetric arrangements are used. An analysis of two distinct non-axisymmetric arrangements and their limitations will be presented and contrasted. One arrangement, the heterogeneous stripwise wall, depends upon the properties of self-assembled monolayers (SAMs) to produce regions of altering wettability [2]. The second arrangement is similar to the stripwise wall, but without the enforced periodicity. Consequently, it should supersede the stripwise wall as a preferred arrangement for line tension measurements on non-fluid substrates.

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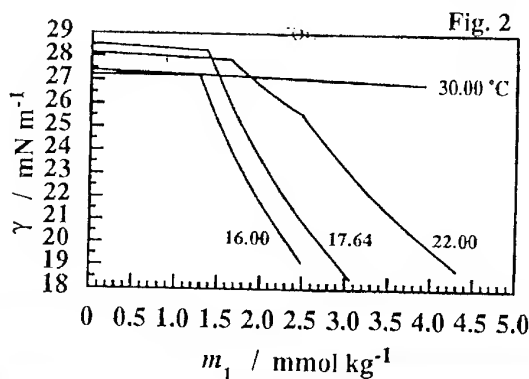
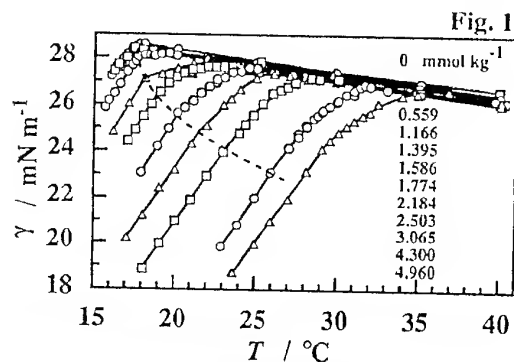
## 137.B1

PHASE TRANSITIONS OF THE ADSORBED FILM OF  
 $F(CF_2)_{12}(CH_2)_{16}H$  AT THE SURFACE OF LIQUID HEXADECANEY. Hayami<sup>1</sup> and G. H. Findenegg<sup>2</sup><sup>1</sup>*Department of Home Economics, Chikushi Jogakuen Junior College, Dazaifu, Fukuoka 818-01, Japan*<sup>2</sup>*Iwan-N.-Stranski-Institut, Technische Universität Berlin, Strasse des 17. Juni 112, Berlin 10623, Germany*

The surface tension  $\gamma$  of the hexadecane solution of semifluorinated alkane, pentacosafuorooctacosane  $F(CF_2)_{12}(CH_2)_{16}H$  (abbreviated as  $F_{12}H_{16}$ ), against air was measured as a function of temperature  $T$  at constant molality  $m_1$  under atmospheric pressure. The surface tension value is plotted against temperature in Fig. 1. Clearly, all the curves are seen to have a break point; this indicates that a phase transition takes place at the surface of hexadecane and in the adsorbed film of  $F_{12}H_{16}$ .

The surface tension vs temperature curves of hexadecane and of the very low concentrations of  $F_{12}H_{16}$  are composed of two almost linear curves, and coincide with each other below the break point temperature. Therefore the curves have only one break point. There are three regions on the other curves in Fig. 1, namely, high temperature region having an almost linear and a negative slope, medium temperature region having an upward concave curvature, and low temperature region having an almost linear and a positive slope. Therefore there are two kinds of break points among the three regions in the high concentration of  $F_{12}H_{16}$ . These two types of the break points are connected by the three dotted lines.

The  $\gamma$  value at a given temperature was read from Fig. 1 and plotted against  $m_1$  in Fig. 2. The slope of the curve is found to change remarkably at the phase transition points. The curve of 16°C has almost no concentration dependence at concentration below the transition point, as can be expected from Fig.



The results have been analyzed by use of thermodynamic equations of adsorption. The thermodynamic quantities associated with the adsorption such as surface density ( $\Gamma_1^H$ ) and entropy change ( $\Delta s$ ) were evaluated and compared with the adsorbed films of other materials that we studied. We concluded that the phase transitions of the adsorbed film of  $F_{12}H_{16}$  take place among the gaseous, expanded, and condensed states. The surface of hexadecane transforms from the gaseous to the condensed state. The surface of hexadecane solution of  $F_{12}H_{16}$  exhibits two types of condensed phases.

### 138.B1 SPONTANEOUS TRANSFORMATION INTO THE EQUILIBRIUM FORM OF CAMPHENE CRYSTALS AS A CAPILLARY PHENOMENON

D. Iwanov and D. Nenow

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Experimental investigations of the spontaneous transformation of a nonequilibrium form to an equilibrium one of camphene crystals were carried out. A single crystal with micron sizes was obtained in a capillary glass ampoule, previously evacuated and sealed off at  $1 \cdot 10^{-6}$  Torr. The changes of the crystal surface were observed and photographed by the optical microscope at several temperatures near the melting point. The temperature was kept constant with an accuracy of  $\pm 0,01^\circ\text{C}$  and the heat field was homogeneous. During the process, the crystal form was changed from an elongated arbitrary form through cylindrical and elliptical ones to a spherical one. The surface area of the consecutive forms decreased to the minimum area of the sphere, having minimum surface free energy. The thermodynamic driving force of the spontaneous isothermal transformation of the crystal is the chemical potential difference between various places of the nonequilibrium crystal surface, respectively their vapour pressure difference. The last difference was determined by the curvatures of the surface, according to the Thompson-Gibbs equation [1]. In this way, the two ends of the crystal having bigger curvature, were evaporated and the middle region of the crystal with a smaller curvature grew. The supersaturation over the growing part of the crystal was determined by the obtained vapour pressure difference. When the curvature became constant over the entire surface, the crystal transformation as well as the action of the capillary effect stopped. The spontaneous transformation of such large crystals into the equilibrium form is a manifestation of the capillary effect. It is possible, analogously to liquids, because of the absence of an energetic barrier for two-dimensional nucleation, owing to the atomically rough structure of the nonsingular surface, existing at the temperatures under investigation [2,3].

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### 139.B1 AGGREGATION NUMBERS AND SURFACE TENSION COMPONENTS OF IONIC SURFACTANT MICELLES

A.V. Konstantinovich and I.A. Konstantinovich

*Chernovtsy State University, 2 Kotsyubinsky Str., Chernovtsy, Ukraine, UA-274012*

Theoretical investigation of spherical micelles formed by surfactant ions with linear hydrocarbon chains at the critical micelle concentration is reported.

Aggregation numbers  $n$  of spherical micelles is calculated according to [1]:

$$n = n_0 \left( 1 + \frac{\Delta r}{l_h} \right)^2, \quad n_0 = \frac{4\pi l_h^2}{3S_R}$$



where  $l_h$  is the total length of the hydrophobic part of the surfactant ion,  $S_R$  is cross-section of surfactant ion chain,  $\Delta r$  is the difference between the radius  $r_h$  of the continuous hydrophobic micelle core impenetrable for water and the total length of the extended hydrophobic part  $l_h$  of the surfactant ion. The theoretically calculated spherical micelle aggregation numbers [1] are in good agreement with the experimental data for the case of  $r_h = l_h$ .

The surface tension  $\sigma$  of the spherical ionic micelles consists of intermolecular and electrostatic components [2]:

$$\sigma = \sigma_G = \sigma_{Gmol} + \sigma_{Ge} = \sigma_{Gmol} + \frac{r_e}{r_G} \sigma_{Ge}, \quad \sigma_e = -\frac{q_m^2}{16\pi\epsilon r^3} \left( 1 - \frac{r_e^2}{(r_e + d + r_D)^2} \right)$$

Here  $\sigma_G$ ,  $r_G$ ,  $\sigma_{Gmol}$ ,  $\sigma_{Ge}$  are the surface tension, the radius, intermolecular and electrostatic surface tension components at the Gibbs tension surface, respectively,  $r_e$ ,  $\sigma_e$  are the micelle radius and electrostatic surface tension component at the level of micelle charges respectively,  $\epsilon$  is the medium permittivity,  $q_m = e_n$  is the micelle charge,  $r_D$  is the Debye screening length,  $d$  is the minimal distance between counterions in the solution and the surface of micellar charge distribution surface.

In this report the intermolecular surface tension component can be considered as the experimentally determined parameter. The value of the electrostatic surface tension component for the ionic spherical micelles, calculated at the assumption that  $r_G = r_h$ , confirm the stability of micelles.

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## 140.B1 THERMODYNAMIC CHARACTERISTICS OF ADSORPTION OF BENZENE DERIVATIVES ON MODIFIED SILICA GELS

S. N. Lanin, M.Yu. Ledenkova, Yu.S. Nikitin

*Laboratory of Adsorption and Chromatography, Dept. of Chemistry, Moscow State University, 119899 Moscow, Russia*

The subject of this work was the investigation of surface properties of the silica gels with chemically bonded aminopropyl and cyanodecyl groups by means of microcolumn high performance liquid chromatography. The experiments were carried out using liquid chromatograph Milichrom with ultraviolet spectrophotometer (wave length 254 nm). n-Hexane and binary mixtures of propanol-2 and tetrahydrofuran with n-hexane were used as a mobile phase (range of concentration of polar component was from 0.005 to 2.5 volume percent).

Chromatographic behaviour of benzene and its derivatives in the normal phase HPLC using two different sorbents - aminopropyl- and cyanodecylsilica (Diasorb 130-NH<sub>2</sub> and Diasorb 130-CN) was used to assess the surface chemistry of investigated sorbents and to study the thermodynamic characteristics of adsorption.

Retention parameters of benzene derivatives were used for the calculation of the standard change in differential free energy of adsorbate ( $\Delta G_0$ ) and equilibrium constants of molecular interactions (taking place in chromatographic system) between molecules of solute and polar component of mobile phase. All these interactions are involved in equation that correlates retention and mobile phase composition [1]. Good agreement between calculated and experimental retention data demonstrates the adequacy of the proposed model.

The comparison of separation of model mixtures of chloride and nitro substituted benzenes demonstrated better efficiency and selectivity of aminopropyl modified silica.

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## 141.B1 TRANSITIONAL BEHAVIOUR OF AMPHIPHILES' ADSORPTION LAYERS AT AIR/WATER AND OIL/WATER INTERFACES

K. Lunkenheimer<sup>1</sup>, A. Goebel<sup>1</sup> and R. Hirte<sup>2</sup>

<sup>1</sup> Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5,  
D-12489 Berlin, Germany

<sup>2</sup> Technische Fachhochschule Wildau, Friedrich-Engels-Str. 63, 15742 Wildau

Investigations of soluble amphiphiles adsorption properties of the air/water interface carried out in recent years made us conclude that their equilibrium surface tension vs concentration isotherms have to be described by a surface equation of state that makes allowance for a transition state in the adsorption layer. The transition state is assumed to continuously connect two adsorption states attributable to two different surface configurations. The width of the transition range depends on the amphiphile's structure. Further evidence for the hypothesis of the transition state could also be provided by laser light scattering and surface potential investigations.

Here we report on studies about the influence of the oil phase on the characteristics of the transitional behaviour and on the resulting differences in the amphiphiles' adsorption properties at the air/water and the *n*-alkane/water interfaces. Prior to the investigations the sodium-*n*-alkane sulfonates (C<sub>7</sub> to C<sub>14</sub>) and *n*-alkanes (C<sub>6</sub> to C<sub>14</sub>) were purified by special measures to guarantee the grade of interface-chemical purity to escape any influence of falsifying impurities.

There is a remarkable difference in the transitional behaviour at the air/water and the alkane/water interface. The width of the transitional region occurring at the former interface is considerably smaller than that revealing at the latter. This behaviour is accompanied by comparatively larger cross-sectional areas of, and noticeably weaker interactions between, the adsorbed surfactant molecules, although it turns out that the surface activity is much stronger for the oil/water interface depending distinctly on the alkanes' hydrocarbon chain length. Even/odd effects are observed not only in the transition and adsorption parameters but even in the interfacial tensions of the pure *n*-alkane/water systems. The surface pressure at the onset of the transitional region depends on the length of the surfactant and the alkane molecule. This result can be understood by the molecular space constraints in the interface.

These findings support the amphiphiles mechanism of adsorption as proposed by us recently. Furthermore, they provide information about the possibility to optimize surfactant efficiency in its application to oil/water systems.

## 142.B1 EFFECTIVE HAMILTONIAN FOR LIQUID-VAPOR INTERFACES

K. R. Mecke and S. Dietrich

Fachbereich Physik, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany

Starting from a microscopic density functional theory for inhomogeneous fluids we derive an effective Hamiltonian for liquid-vapor interfaces of simple fluids that goes beyond the common phenomenological capillary-wave description. Explicit expressions for the surface tension and the bending rigidities of capillary waves of fluid interfaces are given. In contrast to other approaches we take into account the long-ranged power-law decay of the dispersion forces between the fluid particles, which changes qualitatively the functional form of the wavevector-dependent surface tension. In particular, we find two different limiting bending rigidities for the capillary waves, a negative one for small wavevectors determined by the long-ranged dispersion forces and a positive rigidity for large wavevectors due to the distortions of the intrinsic density profile in the vicinity of the locally curved interface. The relevance of these results to the interpretation of scattering experiments and the differences between our approach and the standard capillary-wave theory are discussed. We expect that the prediction of a negative bending rigidity can be confirmed by X-ray scattering experiments.

### 143.B1 ON INCREASED CHEMICAL ABSORPTION OF COMPONENTS OF THE EXPIRATORY AIR ON THE SURFACE OF SEMICONDUCTORS

A.M. Pashaev<sup>1</sup>, G.A. Mamedov<sup>1</sup>, M.A. Talibi<sup>2</sup>

<sup>1</sup>*Institute of Physics, Azerbaijan Academy of Sciences,*

<sup>2</sup>*University Politech, Azerbaijan*

It is determined that under the action of expiratory air flow in near-surface layer of some semiconductors the non-equilibrium electron-hole pairs are generated. In the semiconductors with barrier structure the pairs separate by p-n junction and in the circuit the short circuit current arises. The investigation showed that the short-circuit current increases with the intensity of flow by the linear law. In this case the linear part of the diagram has not saturation and it includes a wide dynamic range. This fact indicates the increased adsorption capacity of the semiconductors under study to the components of the expiratory air. As a result a great amount of the components of the expiratory air is in the generation of the current. Energy develops across as result of chemical interaction of components of expiratory air from the surface of semiconductor. Semiconductor plays part of the catalyst. By this means it is the direct conversion of the chemical energy into the electric energy without destruction of the semiconductor - catalyst. This offers considerable scope for the generation of the scope for the generation of intrinsically semiconductive respiration sensors with p-n junction.

### 144.B1 THERMAL EFFECT DURING MOTION OF GAS BUBBLES IN UNIFORM LIQUID

V.I. Roldughin

*Institute of Physical Chemistry, Russian Academy of Science, Moscow, Russia*

Thermocapillary phenomena are of great importance for nonequilibrium colloidal systems. Interrelation between various thermocapillary phenomena were established using nonequilibrium thermodynamics method. To our knowledge, the problem of cross effect with respect to the thermocapillary motion of droplets or gas bubbles has not been discussed in literature. Based on sufficiently large velocities of thermocapillary motion of droplets and bubbles, one may state that this cross effect must be rather pronounced. The interrelation between the thermocapillary motion of droplets and the cross effect was formally established in [1], where the general phenomenological equations of particle motion in uniform media were derived. It follows from these equations that nonuniform heating (thermal polarization) of medium near bubble moving in a uniform liquid is the cross effect with respect to thermocapillary motion.

For a gas bubble (or droplet of foreign liquid) moving in a uniform liquid with constant velocity  $u$ , the nature of the thermal process is rather simple. When liquid flows around a bubble, a new surface is continuously formed in the front part of the bubble and disappears in the rear part. When the liquid surface is formed, heat is absorbed; when the surface disappears, heat is released. Hence, there is heat sink at the front part of the bubble and heat source at the rear part. The presence of the sink and the heat source results in temperature nonuniformity: the front part tends to be cooled, while the rear part tends to be heated.

The calculation of the temperature field based on heat and mass transfer equations gives the

temperature drop between front and rear parts of a bubble equal to:  $\Delta T = \frac{4T \frac{\partial \sigma}{\partial T}}{(k_g + 2k)} \frac{\beta}{1 + \beta} u$ , here  $\sigma$  is the

surface tension,  $k_g$  and  $k$  are the heat conductivities of gas filling the bubble and liquid and  $\beta$  is the ratio of viscosities of the liquid and gas.

As is seen, the temperature drop is independent of bubble size and is primarily determined by the variation of surface tension with temperature and the velocity of bubble motion. Estimates show that the temperature drop can be determined in experiments.

## 145.B1

PROGRESS IN COLLOID SCIENCE OF WATER:  
SURFACE PROPERTIES AND PHASE TRANSITIONS

A.I. Rusanov

*Mendeleev Center, St Petersburg State University, 199034 St Petersburg, Russia*

The studies of surface properties of water for last decades and the present state of knowledge are summarized. The following problems are involved.

1. The determination of the self-adsorption of liquids from the dependence of surface tension on pressure. The experimental procedure has been elaborated with using helium as the least soluble gas and the first reliable data on the surface density of liquids have been obtained. Water exhibits a larger decrease (up to 15%) in density at the free surface as compared with other liquids. In addition, the maximum of surface density of water is realized at a considerably higher temperature than for water in the bulk.

2. Surface orientation in dipole liquids. Still in 1969 Kuni and Rusanov showed that dipoles of a polar fluid are oriented in parallel to the fluid surface if the dielectric permittivity of the fluid is larger than that of an adjacent phase and perpendicularly to the surface if the dielectric permittivity of the fluid is smaller than that of an adjacent phase. Applied to the liquid/vapor equilibrium for water as a dipole liquid, this means that the orientation of water dipoles should change from vertical to horizontal when moving from the vapor to the liquid, being horizontal at an average. Recent molecular dynamics simulations giving the orientation distribution functions for water dipoles and HH-vectors confirm this picture.

3. Effect of an electric field on the surface tension of polar liquids. The solution of the problem is explained at an arbitrary direction of an electric field with respect to the water surface. The most striking result is that the mechanical surface tension and the thermodynamic surface tension of a liquid are different in the presence of an electric field similarly to the case of a solid, the influence of an electric field on the mechanical and thermodynamic surface tensions being also different.

4. Nucleation on charged particles. The interaction of an electrical field with the surface polarized layer of water leads to the effect of the charge sign (which was unknown in classical Thomson's theory of nucleation on charged particles) on the work and the activation energy of nucleation. Being applied to the natural processes of phase transitions of water in the atmosphere, this effect supplies the thermodynamic explanation of the origin of the atmospheric electricity.

5. Condensation of water on macroscopic nuclei. The possibility of the water condensation at extremely small supersaturations can be secured by two different mechanisms of heterogeneous condensation. The first is the widely known effect of solubility of a nucleus in the process of condensation (e.g., condensation on salt particles). The second mechanism originates from the disjoining pressure of a thin film of water on an insoluble nucleus. The theory has been developed up to numerical estimations which yield rather low values (say, 0.03) for critical supersaturation. This allows the explanation of the water condensation processes at low supersaturations in the atmosphere.

## 146.B1

SURFACE TENSION OF MIXTURES OF  
METHANOL+CYCLOHEXANE CLOSE TO THE UCSTLuis M. Trejo<sup>1</sup> & Ian A. McLure<sup>2</sup><sup>1</sup> *Laboratorio de Termodinámica, Facultad de Química, U.N.A.M., Mexico, D.F. 04510 Mexico.*<sup>2</sup> *Dep. of Chemistry, University of Sheffield, Sheffield S3 7HF England*

We studied the liquid-liquid equilibrium and the surface tensions of mixtures of methanol + cyclohexane in orthobaric conditions as function of mole fraction of methanol  $X_1$  and temperature close to the Upper Critical Solution Temperature (UCST). We used commercial cyclohexane (Aldrich of purity 99.9 + %) and methanol (Aldrich of purity 99.9 + %) without further purification. We measured phase separation temperatures  $T_{sep}$  on degassed mixtures using a calibrated platinum resistance thermometer. With the 18 obtained  $T_{sep}$  we estimated the UCST 45.50 °C at  $X_1 = 0.49$ , which indicates a mole fraction of water of  $4.3 \times 10^{-4}$  in our system (J.Chem.Thermodyn. 20, 439-445 (1988)). Surface tensions  $\sigma$  were measured on degassed samples of the pure components and the mixtures with a cell containing four calibrated Veridia glass capillaries using the capillary rise method: The squared capillary constant  $a^2$  was obtained as the

gradient of the plot  $(h_j + r_j/3)$  vs  $(1/r_j)$  where  $h_j$  and  $r_j$  are the capillary high and radii of a given  $j$  capillary glass. The surface tension was calculated from the equation  $\sigma = a^2 \rho g / 2$ , where  $g = 981.342 \text{ cm/s}^2$  at Sheffield and the density  $\rho$  was obtained from the literature for the pure components (J.Chem. Thermodyn. 20 1089-1096 (1988)) and the mixtures (J.Chem. Thermodyn. 19 949-957 (1987)). The mixture is normal in the sense that the more volatile component, methanol, has the lower surface tension: we obtain for methanol  $\sigma = 24.304 - 0.086t$  and for cyclohexane  $\sigma = 27.190 - 0.117t$ , with  $\sigma$  in mN/m and  $t$  in C in the interval 25-65 C. Reflecting the occurrence of marked positive deviations from bulk-phase ideality in the mixtures the isotherms  $\sigma$  vs  $X$  obtained from 40 to 55 C display marked negative deviations from surface ideality with a minimum occurring at higher  $X_1$  as the temperature is increased. Two isotherms closer to the UCST (46 and 48C) show the characteristically flat portion which is larger for the one at 46C. The results are analyzed in terms of the regular solution theory and the total surface segregation concept.

## 147.B1

### CAPILLARY CONDENSATION AND MOLECULAR STRUCTURE OF METHANE IN ANTHRACITE PORES

Aleksey Vishnyakov, Elena M. Piotrovskaya and Elena N. Brodskaya  
*St. Petersburg State University, Department of Chemistry, Universitetsky pr. 2,  
198904 St. Petersburg, Russia*

The results of grand canonical Monte Carlo simulation of methane in slit anthracite pores are presented. The atomic structure of the adsorbent surface, is considered to be energetically heterogeneous with various carbon, nitrogen, oxygen and sulphur atoms as well as vacancies taken into account. The influence of the microscopic structure of coal on the vapour-liquid phase coexistence and the molecular structure of the adsorbate for the pores with the widths  $H$  from 7.6 to 37.7 Å was studied. It has been found that the phase diagram for methane in pores with heterogeneous walls is shifted significantly both from that of the bulk systems and for methane in the corresponding pores where adsorbent is modelled as a continuum. Local density and local energy profiles as well as the distribution of methane along the surface of the adsorbent in the first adsorbed layer has been obtained for the temperatures  $T = 112.5$  and 300K.

## 148.B1

### ANCHORING TRANSITION AT A NEMATIC LIQUID CRYSTAL-SUBSTRATE INTERFACE

A.V. Zakharov  
*St. Petersburg Institute for Machine Sciences, RAS, St. Petersburg, 199178, Russia*

Among the surface properties of liquid crystals (LCs) which have been a subject of intense interest for many years, one, known as anchoring, plays a crucial role in the fabrication of LC displays. The interfaces at which anchoring has been mostly studied are those with solid substrates [1]. Although many attempts have been made to theoretically describe the anchoring of nematic LCs, however, the underlying physical mechanisms are not yet fully understood.

Recently a kind of Be the theory, which takes account of intercell pair correlation for describing NLC systems composed of interacting ellipsoidal molecules near an interacting wall has been proposed [2]. But in this approach, only one orientation of the director, parallel to the surface (homogeneous anchoring) has been investigated.

The aim of the present work is to extend the above approach in order to describe not only homogeneous anchoring, but investigate the question of which orientation of the director

$$\gamma_{tilt} = \cos^{-1}(\vec{n} \cdot \vec{k}),$$

where  $\vec{n}$  is the director and  $\vec{k}$  is the normal vector to the surface, minimizes the Helmholtz free energy.

Calculations have been carried out for cubic close packing with the nearest-neighbor Gay-Berne inter-molecular potential and with a (9-3) like orientation-dependent molecule-wall interaction. The equilibrium surface free energy profiles and different type of anchoring transitions have been calculated.

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## 149.B1

### MOLECULAR DYNAMICS SIMULATIONS OF SURFACE PROPERTIES OF WATER AND METHANOL MICRODROPLETS

Viktor V. Zakharov<sup>1</sup>, Elena N. Brodskaya<sup>1</sup>, Aatto Laaksonen<sup>2</sup>

<sup>1</sup>Department of Chemistry, St. Petersburg University, 199034 St.Petersburg, Russia

<sup>2</sup>Division of Physical Chemistry, Arrhenius Laboratory, University of Stockholm, Stockholm,  
S-10691, Sweden

Microdroplets of water and methanol are investigated by computer simulations method. Molecular models by Jorgensen et al. are used for both substances. Local properties such as density, energy, electric potential and pressure are calculated for droplets of different size.

The surface potential of liquids is evaluated on the basis of electric potential profiles. The value of the surface potential is found negative for both water and methanol. It is shown that the molecular quadrupole moment gives a significant contribution to the surface potential as for water and methanol. For both liquids, the orientational distribution functions show that the vectors of dipole moments are almost parallel to the dividing surface.

The surface tension of droplets is estimated and its dependence on the droplet size is investigated. It is obtained that the surface tension of microdroplet is increasing monotonously with the droplet radius. In the considered range of droplet size the surface tension has not reached the value for the plane interface. In the case of water the largest value calculated is about 55 mN/m, being considerably lower than the experimental value. For methanol droplets the surface tension approaches 20 mN/m, reasonably close to the experimental value.

## 150.B2

### THE SHAPE OF ELECTRONIC ABSORPTION BANDS IN EPITROPIC LIQUIDCRYSTALS

Afanas'eva A.A., Mikhailenko V.I., Popovskiy A.Yu., Popovskiy Yu.M.

Odessa Marine Academy and Marine University, Odessa, Ukraine

Action of solid substrate surface on the wall-adjacent layers of organic liquids with anisometric molecules can lead to formation of orientationally ordered boundary phase so called epitropic liquid crystal (ELC). Transition from vapour phase to condensed one (liquid and further to ELC) causes the changes of electronic absorption band parameters (such as shape, halfwidth, position of the maximum).

It was proposed the theoretical model in order to study these changes. The main assumptions of the model were: a) the shape of the band in the vapour phase can be described by the Edjvort function with the nonzero third central moment; b) expansion of the intermolecular interaction energy into the series of Legendre polynomes contains the additives of zero, second and fourth orders.

The shape of the absorption band in the isotropic liquid phase was found by averaging of the Edjvort function with the help of a distribution function that contains the additive only of the zero order. In order to make the proper description of the band shape in the ELC phase we had to take into account the additives of the second and the fourth order which are connected with the order parameter  $S_2$  and the dispersion  $S_4$  accordingly.

The model was compared with experiment on the example of intermolecular charge transfer band of nitrobenzene ( $V_m=38000 \text{ cm}^{-1}$ ). The band asymmetry increases when the transition from vapour to isotropic liquid and further to ELC phase takes place. Besides, there was observed the decreasing of the band half-width and the bathochromic (long-wave) shift of the maximum position with the decreasing of the ELC,

phone layer thickness  $h$ . The frequency shift dependence vs the thickness is approximately reciprocal quadratic,  $-dN \propto 1/h^2$ .

The observed transformations of the ELC phase spectra was described in frames of proposed model - taking into account the thickness dependence of the corresponding parameters that define the function of the band shape. It was found that the order parameter  $S_2$  does not depend practically on the ELC layer thickness and also that the dispersion  $S_4$  decreases when the ELC layer thickness decreases. The last fact testifies that the increasing of the potential of the surface forces field in turn causes the increasing of the degree of the orientation order of the system.

## 151.B2 THERMODYNAMICS OF INTERACTING CURVED INTERFACES IN THIN LIQUID FILMS AND FLUID PARTICLES OF COLLOIDAL SIZE

Valery Babak

*IDEOS RAS, 28 Vavilova str., Moscow 117813 Russia*

The studies on the thermodynamic of fluid particles of colloidal size (micelles, vesicles, microemulsions and coacervate phase droplets, etc.), microscopic thin liquid films and membranes, and interaction between colloidal particles and interfaces, are systematically reviewed on the base of the elaborated thermodynamics of interacting curved interfaces.

The elaborated thermodynamics is a self-consistent and closed system of concepts and equations relating the disjoining pressure in thin liquid films to other thermodynamic parameters and functions. This thermodynamics generalized both, the Gibbs' thermodynamics of free curved dividing surfaces and the thermodynamics of plane-parallel thin liquid films, in corresponding regions of definition.

Different approaches to the definition of the interfacial tension for fluid colloidal particles and its dependence on the radius of curvature of the dividing surface are discussed. The fundamental equilibrium equations for systems containing curved interacting interfaces, including the transition region of thin liquid films and membranes, and colloidal particles, are obtained. The possibilities of the elaborated thermodynamics in describing aggregative stability of emulsions (in general, disperse systems with deformable particles), wetting and adhesion phenomena, rheological properties of highly concentrated colloidal systems, is illustrated by numerous examples.

## 152.B2 STUDY OF LIQUID CRYSTALS PRE-WETTING FILMS

S. Bardon<sup>1,2</sup>, M.P. Valignat<sup>1</sup>, H. Dumoulin<sup>3</sup>, R. Ober<sup>1</sup>, A.M. Cazabat<sup>1</sup>

<sup>1</sup>*Laboratoire de Physique de la Matière Condensée, Collège de France, Paris, France*

<sup>2</sup>*Laboratoire Central de Recherche, Thomson-CSF, Orsay, France*

<sup>3</sup>*Laboratoire de Physique des Solides, Orsay, France*

The anchoring and wetting properties of liquid crystals are closely related to the organization of the molecules in contact with the solid surface. We study this organization in the pre-wetting films of liquid crystals micro-droplets by combining ellipsometry, x-ray reflectivity, and atomic force microscopy. We present results obtained on the 4-n-octyl-4'-cyanobiphenyl (8CB) spreading on bare silicon wafers.

With ellipsometry, the measured thickness of the 8 CB pre-wetting film is of 45 Å and remains constant while the temperature changes from 5°C to 65°C. In this temperature range, 3 phase transitions occur in the macroscopic part of the drop: solid to smectic A at 21°C, smectic to nematic at 33°C, and nematic to isotropic liquid at 40°C. This results, compared with systems in which 2D phase transitions occur, lead to information on specific interaction in the film.

With X-ray reflectivity we measure a modulation of the electron density in the film along the normal to the substrate. It shows that molecules are well ordered in the film and we propose a model in which a smectic like bilayer lies on a monomolecular layer. This model agrees with the thickness measured by ellipsometry. Furthermore, this organization is still observed when the length of the alkyl part of the molecule is changed ( $n=5,8,10$ ).

Finally, it is possible to perform atomic force microscopy in tapping mode on this film. With 8CB we observe new details on the edge of the pre-wetting film like small fingers and get information about the roughness of the film. With more visquous coumpouds the organization in the first smectic layer depends on the substrate and it is possible to determine tilt angles from AFM measuements.

## 153.B2

### SURFACE FORCES IN WETTING PHENOMENA

N.V. Churaev and V.D. Sobolev

*Institute of Physical Chemistry, Moscow, Russia*

Stability of colloids and wetting films on solid surfaces may be considered in a similar way on the basis of the theory of surface forces. The theory gives the equilibrium distance between particles, while equilibrium between wetting films and bulk liquid is characterized by the contact angle  $\theta$ . Frumkin and Derjaguin have shown that the latter is interconnected with the isotherm of disjoining pressure of wetting films,  $\Pi(h)$ . In distinction from colloids, wetting film represents a nonsymmetrical system bounded by two different bulk phases. In this case electrical potential of solid-liquid and liquid-gas interfaces may be different not only by value but also by sign, causing the forces of electrostatic attraction. We have calculated the  $\Pi(h)$  isotherms for aqueous electrolyte and surfactant solutions taking into account molecular, electrostatic and structural forces. Wide range of electrical potentials, Hamaker constants and parameters of structural forces of hydrophilic repulsion and short-range hydrophobic attraction was used for this purpose. As a first step, the equilibrium thickness  $h$  was calculated as a root of equation  $\Pi(h)=0$  expressing the algebraic sum of all the components of disjoining pressure. After that it was possible to calculate the contributions of different components of the free energy of wetting film into the value of contact angle. It was shown that complete wetting may be attained due to predominant action of structural repulsion forces caused by presence of surface centres that are able to form hydrogen bonds with water molecules. Large contact angles arise due to predominant action of hydrophobic attraction, forces and/or electrostatic attraction forces. The latter effect is characteristic for ionic surfactant solutions. At a moderate degree of hydrophilicity, that is in the range of  $\theta$  from  $15-20^\circ$  to  $50-60^\circ$  it is sufficient to take into account the molecular and electrostatic forces only. This determines the region of applicability of die DLVO theory in wetting phenomena. However, the values of parameters that characterize the structural forces are not well known. Due to this the results of calculations give a roughestimation of contact angles. Like in the case of direct force measurements between two model bodies, experimental values of  $\theta$  may be rather used for evaluation of parameters of structural forces in the nonsymmetrical case of wetting films. The preliminary results have shown that the order of the parameters seems to be the same as in colloidal systems.

## 154.B2

### THERMOCAPILLARITY INSTABILITY OF FLUID SHEETS

L.A. Dávalos-Orozco

*Inst. de Investigaciones en Materiales, Univ. Nac. Autónoma de México, Apartado Postal 70-360,  
Coyoacán, 04510 México D.F., Mexico*

In this paper we investigate the linear thermocapillary instability of a viscous fluid sheet, that is, a thin fluid layer in motion through a gas with two deformable free surfaces. It is supposed that the fluid sheet is moving with constant velocity through a gas in which a temperature gradient is imposed. Therefore, a temperature gradient is developed inside the thin fluid sheet which generates tangential shear stresses at the two free surfaces resulting in Marangoni convection. This phenomenon arises in addition to the isothermal instability due to the displacement of the sheet through the gas which is only affected by viscosity and surface tension. Here, the buoyancy of the sheet is neglected.

This temperature gradient may occur inside a combustion engine where fuel is injected in the form of a fluid sheet which eventually, due to a breakup process, will transform completely into droplets. The size of these droplets is supposed to be determined by the most unstable wavenumber of the fluid sheet perturbation.



The results of this paper generalize those obtained by Li and Tankin [1] for the isothermal fluid sheet and those of Funada [2] for the Marangoni instability of a thin liquid sheet at zero velocity. From the combination of these two problems the new set of parameters become the Weber number, the Ohnesorge number, the gas liquid density ratio, the Biot number, the Prandtl number and the Crispation number which, however, depends on the Ohnesorge number and the Prandtl number. Here, two kinds of instabilities are investigated, the antisymmetrical and symmetrical disturbances in which the two free surfaces waves are in phase and out of phase by 90 degrees, respectively. Due to the variety of parameters, the results will be limited to representative values of some of them and change the others.

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## 155.B2

### THIN LIQUID FILM AS A TOOL FOR MANIPULATION AND STUDY OF MICRO- AND NANOPARTICLES

N.D. Denkov<sup>1</sup> and K. Nagayama<sup>2</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry,  
Sofia University, 1126 Sofia, Bulgaria

<sup>2</sup>Department of Life Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153, Japan

The thin liquid film, forming between two air bubbles in a foam or between two drops in an emulsion, has been recognised for many years as the most important structural element in disperse systems with respect to their stability. Our recent studies show that under appropriate control the liquid film can be successfully used as a tool for manipulation and study of micrometer or nanometer sized particles, due to its ability to spontaneously maintain a constant thickness throughout large area. Three specific examples will be discussed. First, the liquid films were used as a matrix for the formation of well ordered two-dimensional arrays (colloid crystals) from latex spheres (1). The experiments demonstrated that the process of particle ordering takes place only when the film thickness is comparable with the particle diameter. By appropriate control of the film adius and of the water evaporation from the film, we were able to produce arrays containing different number of particle layers. Thin particulate layers have peculiar optical properties, which strongly depend on the layer thickness and on the particle size, shape and arrangement. Thus our method provides the unique possibility for controlled production of appropriate samples for optical studies. Second, we developed (2) a novel method for ultra-rapid freezing (vitrification) of aqueous films containing an ordered monolayer of particles - lipid/protein vesicles, latex spheres, micelles or viruses. These samples are particularly suitable for investigation by cryo-electron microscopy at liquid nitrogen temperature because an image averaging over many particles is possible for improvement of the resolution. The third example is the recently developed method for determination of the three-phase contact angle of micrometer sized particles (3). In this method a single particle (solid or fluid) is entrapped within a liquid film of equilibrium thickness smaller than the particle diameter. A liquid meniscus is formed around the particle, and observations in reflected light (when an interference pattern is discernible) allow to restore the meniscus shape and to determine the three-phase contact angle.

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## 156.B2

LINE TENSION EFFECT ON AILKANE DROPLETS  
NEAR THE WETTING TRANSITIONA. D. Dussaud<sup>1</sup> and M. Vignes-Adler<sup>2</sup><sup>1</sup>Department of Chemical Engineering, Princeton University, Princeton NJ 08544<sup>2</sup>Laboratoire des Phénomènes de Transport dans les Mélanges du CNRS, 4 ter, Route des Gardes,  
F 92190 Meudon, France

We have investigated n-octane droplets resting on the surface of sodium chloride solutions as a function of the salt concentration in a saturated, closed cell. For high salt concentration, the system approaches a wetting transition: the contact angles are very small ( $\sim 1^\circ$ ), the macroscopic droplet is unstable, and it breaks up spontaneously into microdroplets. The stable polydisperse population of microdroplets ( $5\mu\text{m} < r < 250\mu\text{m}$ ) allowed us to analyze the dependence of the contact angle on droplet size. Because of the low contact angle values, accurate measurement of contact angles was obtained by interferometry. Moreover the accuracy of the classical method was significantly improved through the systematic use of three wavelengths. The relationship between the contact angle and the droplet size indicated a positive line tension,  $\tau$ , and the order of magnitude of  $\tau$  was in good agreement with the theoretical prediction.  $\tau$  varies between  $(8.6 \pm 0.9)10^{-11}$  N and  $(1 \pm 0.1)10^{-9}$  N and was dependent on the salt concentration. The positive sign of  $\tau$  and the significant effect on droplet shape were related to the fact that the system was approaching the wetting transition.

## 157.B2

DIFFUSION OF CO<sub>2</sub> IN WATER

Marc in het Panhuis and Charles H. Patterson

Physics Department, Trinity College, Dublin, Ireland

The theory group at Trinity College Dublin has been interested in foams for many years (e.g. Weaire and Rivier (1984)). One of the unresolved problems is related to diffusion of small gaseous molecules (e.g. CO<sub>2</sub>, N<sub>2</sub>) through thin water and surfactant films. Using software developed by Daresbury Laboratory (Smith (1995)), we started to model bulk water systems with the SPC/E water model (Berendsen et al. (1987)) reproducing the radial distribution function, diffusion constant, density, potential energy and liquid structure of real water. We present an effective pair potential for rigid carbon dioxide in liquid water. It assumes point charges and Lennard-Jones interactions centered at each atom. Molecular Dynamic simulation show that CO<sub>2</sub> diffuses in water through jumps. These jumps make it difficult to calculate the diffusion coefficient of CO<sub>2</sub> in water. We have begun to analyse these jumps and their effect on the diffusion coefficient.

This work was supported by the EU Mobility Programme, MihP was an HCM Fellow, Contract ERBCHBGCT 940520. We would like to thank Hitachi Dublin Laboratory for provided computer time and R. Lynden-Bell for many useful discussions.

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## 158.B2 LATERAL CAPILLARY FORCES BETWEEN PARTICLES ATTACHED TO INTERFACES: MEASUREMENT AND PHYSICAL IMPORTANCE

Peter A. Kralchevsky, Vesselin N. Paunov and K. Nagayama

Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics Faculty of Chemistry, University of Sofia, 1 James Bourchier Avenue, Sofia 1126, Bulgaria

The lateral capillary forces originate from the overlap of the menisci formed around particles attached to a liquid interface. When the particles are captured in a liquid film, the deformations are related to the wetting properties of the particle surfaces. In such a case the lateral capillary forces can be essential even for particles of size 10 nm and have been employed for obtaining two-dimensional arrays of globular protein macromolecules and other colloidal particles.

We measured attractive particle-particle and particle-wall lateral capillary force as a function of the separation distance. The "particles" were vertical thin glass cylinders and/or small glass spheres, protruding from an air-liquid interface. To detect the force we constructed a precise torsion microbalance [1]. It is based on counterbalancing the moment of a couple of forces, acting between two couples of particles, by the torsion moment of a thin platinum wire. The experimental results agree well with the theory of the lateral capillary forces.

The inclusions in a phospholipid membrane (say membrane proteins) also cause local deformations, whose overlap gives rise to a special kind of lateral capillary force. To calculate it we developed an appropriate model of a lipid bilayer, which has been described as an elastic layer (the hydrocarbon chain region) sandwiched between two Gibbs dividing surfaces (the two headgroup regions) [2]. The range of interactions turns out to be of the order of dozens of nanometers. The results are in qualitative agreement with the experimental observations.

Interactions of much longer range are observed between latex particles attached to a lipid vesicle. In this case the curvature and the finite area of the vesicle surface become important. This stimulated us to develop a special theory of the capillary interactions between particles attached to a spherical interface [3]. The numerical results show that the capillary interaction can be much larger than the thermal energy  $kT$  and can induce aggregation and ordering of submicrometre particles.

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## 159.B2 GAS PERMEABILITY AND SURFACTANT ADSORPTION AT THE FILM SURFACES

R. Krustev and H.J. Müller

Max-Planck Institut für Kolloid- und Grenzflächenforschung, Berlin, Germany

In our previous works [1,2] it was found that gas permeability of black foam films prepared from aqueous solutions of sodium dodecyl sulfate and different electrolytes (NaCl or LiCl) strongly depends on the film type - CBF or NBF. It was shown that gas permeability of NBF depends on the surfactant concentration. To explain these different results earlier theoretical approaches [1] were combined with a new theory of adsorption layer density at interacting surfaces [3]. This theory takes into account the influence of the interaction between the film surfaces on the chemical potential of the surfactant in the *surface excess phase* (SEP) of the film. This results in an increase of adsorption if the film thins under action of attractive forces between the film surfaces. In the case of film thinning against repulsive disjoining pressure the adsorption should decrease according to the theory. The chemical potential of the SEP of a normal surface (of a bulk solution) is given by

$$\mu_i^s = -S^{so}T / \Gamma^\infty + RT \ln x_i - \sigma / \Gamma^\infty \quad (1)$$

where  $S^{so}$  is excess entropy in the standard state  $\Gamma_{\text{surface}} = 0$ ;  $\Gamma^\infty$  - saturation adsorption;  $x_i$  - molar ratio of the component  $i$  in the SEP;  $\sigma$  - surface tension.

To meet the special requirements of the SEP in an film with interacting surfaces we have to take into account first the modification of the surface tension by the interaction. This is done by introducing in (1) the terms  $\Psi/2\Gamma^\infty$  and  $\delta\P/\Gamma^\infty$

with 
$$\Psi = \int_h^\infty \Pi(h') dh' \quad \text{and} \quad \delta = \bar{v} \Gamma^\infty$$

where  $\bar{v} = \sum v_i \Gamma_i / \Gamma^\infty$  is the molar volume of component  $i$ ;  $\Pi$  - disjoining pressure in the film;  $h$  - film thickness and  $\Gamma_i$  - adsorption of component  $i$ .

Second it has to be taken into account that the saturation adsorption becomes a function of the film thickness in going from the surface of a bulk phase to the interacting surfaces of a film. Therefore, replacing  $\Gamma^\infty$  in (1) according to

$$\Gamma^\infty(h) = \Gamma^\infty / Z(h) \quad \text{with} \quad Z(h) = \frac{TS^{so} + \sigma''}{TS^{so} + \sigma'' + \Psi/2 + \Pi\delta}$$

it results for the chemical potential of component  $i$  in the SEP of the film

$$\mu_i^{sf}(h) = RT \ln \left\{ \Gamma_i(h) / \Gamma_i^\infty \right\} - Z(h) / \Gamma^\infty (S^{so}T + \sigma + \Psi/2 + \Pi\delta)$$

From this we obtain a relation for the adsorption of component  $i$  depending on film thickness

$$\Gamma_i(h) = \Gamma_i(\infty) \exp \left\{ \frac{(\sigma'' - \sigma)(Z(h) - 1)}{RT\Gamma^\infty} \right\} \quad (2)$$

Eqn. (2) enable us to calculate the adsorption density of different states of the film. These results are correlated with permeation data. It is observed that in the range of electrolyte concentration where change in the film type is occurred adsorption jumpwise increase and film permeability decrease. The results show that gas permeation through black films is mainly determined by the properties of the surfactant layers. This properties strongly depend on the interaction forces between two film forming adsorption layers.

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## 160.B2 EFFECT OF THICKNESS NON-HOMOGENEITY ON THE KINETIC BEHAVIOUR OF MICROSCOPIC FOAM FILMS

E. Manev, R. Tsekov and B. Radoev

Department of Physical Chemistry, University of Sofia, 1126 Sofia, Bulgaria

Previous experimental studies have shown that microscopic horizontal foam films do not obey the formulae derived to describe their drainage, applying both planar as well as dimpled film models. The actual dependence of the thinning rate on film size is much weaker than theoretically required. For example, instead of being inversely proportional to the square of film radius, as required by the extensively used Reynolds equation, the experimentally studied films exhibit linear dependence of thinning rate on the film radius  $r_f$  to the power of ca.-0.8, in a wide range of  $r_f$  from 0.05 to 1.0 mm.

In the present work, the effect of thickness non-homogeneity on the drainage of microscopic horizontal foam films was studied experimentally and theoretically. Quasi-static and asymmetrical distribution of thickness irregularities over the film surface was established in the experiment. Such a type of dimpling was modelled theoretically and employed to derive a new equation for the film thinning. This

equation differs from the theoretical expressions known from the literature and is in quantitative agreement with the experimentally determined functional dependence of thinning rate on film size ( $r_f^{-4/5}$ ).

## 161.B2 MOTION OF THE FRONT BETWEEN THICK AND THIN FILM: HYDRODYNAMIC THEORY AND EXPERIMENT WITH VERTICAL FOAM FILMS

V. Paunov<sup>1</sup>, S. Stoyanov<sup>1</sup>, E. Basheva<sup>1</sup>, A. Mehreteab<sup>2</sup> and G. Broze<sup>3</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

<sup>2</sup>Colgate-Palmolive R & D, Inc., Avenue Du Parc Industriel, B-4041 Milmort, Belgium

<sup>3</sup>Colgate-Palmolive Co., Technology Center, 909 River Road, Piscataway, New Jersey 08854-5596

The motion of the front between thick and thin foam film formed in a vertical frame is studied both experimentally and theoretically<sup>1</sup>. We present experimental data for the drainage of vertical foam film stabilized by sodium dodecyl sulfate. The rate of motion of the front turns out to be *constant* for a given electrolyte concentration. Another important quantities that are measured are the thickness of the black film and the jump of the film tension, when the front reaches the bottom meniscus. The rate of the front is proportional to the additional tension (the driving force) regardless of the amount of added electrolyte.

The theoretical model we developed allows quantitative interpretation of the experimental data for the additional tension (the driving force) and the velocity of the front motion. It is demonstrated that the motion of the front "thick-thin" film is accompanied with the formation of steady capillary waves in the transition zone. We show that the energy dissipation in the film is concentrated mainly into the latter part of the transition zone. The study can be helpful for the understanding of the mechanism of the foam film drainage as related to the stability of foams.

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## 162.B2 STATIC AND DYNAMIC FILM TENSION OF THIN LIQUID FILMS FROM DIFFERENT SURFACTANT SYSTEMS

D. Platikanov, M. Nedyalkov, N. Rangelova

Department of Physical Chemistry, University of Sofia, Bulgaria

The behaviour of a small bubble with black foam film on its top (floating on the aqueous solution surface) has been studied during the spontaneous diminishing of the bubble. The surfactant solution surface tension has been determined by another method: A semibubble is obtained on the orifice of a fine capillary tube; its size can be changed by controlled increase or decrease of the gas pressure in the tube; the film tension is determined from the measured curvature of the foam film and the capillary pressure across the film. Experiments have been performed with two different types of surfactants: i) A typical foaming agent - the sodium dodecylsulfate; ii) A complicated biological mixture of natural lipids and proteins - the alveolar surfactant, which covers the surface of the lung alveoli. The results show very different behaviour of these two surfactant systems. The film tension is constant for black films from sodium dodecylsulfate in dynamic conditions, but it changes essentially for the films from lung surfactant. The kinetics of spontaneous bubble diminishing is very different for sodium dodecylsulfate and lung surfactant as well. The results are discussed in connection with the structure of the thin liquid films, including bilayer films, and the surface forces which determine their stability.

## 163.B2 THE INFLUENCE OF SURFACE AGEING ON THE DRAINAGE OF FOAM FILMS STABILIZED BY AQUEOUS SOLUTIONS OF ETHYL (HYDROXYETHYL) CELLULOSE

E. Poptoshev, Suh-Ung Um and R.J. Pugh

*Institute for Surface Chemistry, Box 5607, S-114 86, Stockholm, Sweden*

The drainage times of microscopic horizontal foam films stabilised by dilute aqueous solutions of ethyl (hydroxyethyl) cellulose (EHEC) was shown to be dependent on the ageing effects (conformation changes of the adsorbed macromolecules) occurring in the freshly created air/solution interface. Although these ageing effects could not be directly related to surface tension data, diffusion coefficients were calculated from interfacial tension profiles using classical diffusion theory. As the concentration of polymer increased, the diffusion coefficient was shown to decrease and was considerably smaller than previously reported experimental values determined in bulk solution by NMR. This difference between experimental and theoretical results endorsed a kinetic rather than a diffusion or mass transport model for the transfer of EHEC molecules to the interface. The increase in drainage times with extended ageing times could be explained by the gradual formation of a steric energy barrier caused by configuration changes of the adsorbed polymer. This probably involved the progressive extension of the EHEC tails into the aqueous phase increasing the disjoining pressure, decreasing the drainage rate and producing thick stable films.

## 164.B2 PATTERNS FORMATION IN THIN LIQUID FILMS AND MEMBRANES

D. Gallez, E. Ramos de Souza and T. Erneux

*Université Libre de Bruxelles, Faculté des Sciences Campus Plaine, CP231, 1050 Brussels, Belgium.*

Thin (macroscopic) liquid films display a variety of interesting dynamical behaviours [1], such as film rupture, pattern formation or wave propagation. They find applications in chemical engineering as well as in biology. Amongst the different types of instabilities developed in thin films, deformational instabilities are concerned with spatio-temporal evolution of the local film thickness. Until now, the possibility of the appearance of organised behaviour (dissipative structures) in such systems have received few attention. Indeed, for ultrathin layers (100-1000 Å), long-range molecular forces due to van der Waals attraction usually lead to film rupture. However the presence of repulsive forces of different origins (electrical, hydration or steric) can stabilize the film against rupture and lead to the formation of a new stable stationary state (periodic pattern). These nano-structures are observed in dewetting experiments (nanodrops) [2,3] or in cell/cell or, cell/solid support interactions (periodic contacts of the order of 1 µm) [4-6], or also in lipid vesicles adhering to a solid. Recently, we analyzed whether the emergence of such patterns is confirmed by a theoretical approach. A bifurcation analysis was performed [7] which allows to predict the existence of such structures and to determine the range of parameters for their occurrence. Numerical solutions of the nonlinear evolution equation allowed to describe finite-amplitude deformation. In some conditions, the simulations predict that the thin film undergoes a "morphological phase separation" where nanodrops of the fluid attain equilibrium with flat thin films; this phenomena cannot be predicted by a linear theory. At each step, comparison with experimental data confirms the validity of the dynamical approach to analyse the appearance and the dynamics of patterns in thin liquid films and membranes.

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## 165.B2

## THE SHAPE OF FILMS AND PLATEAU BORDERS IN A FOAM

M. Emilia Rosa<sup>1</sup>, V. E. Fradkov<sup>2</sup> and M. A. Fortes<sup>1</sup><sup>1</sup> *Departamento de Engenharia de Materiais, Instituto Superior Técnico, Lisboa, Portugal*<sup>2</sup> *Materials Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, USA*

Equilibrium of a thin liquid film is analysed in terms of repulsive forces between the two surfaces (liquid-gas interfaces) of the film. These forces equilibrate the curvature and hydrostatic pressure forces. They can be taken into account by defining a film tension,  $\gamma$ , dependent on film thickness,  $x$ .

The Laplace equation for the film shape with variable  $\gamma(x)$  is written and integrated for the no gravity case with appropriate boundary conditions. The shape of Plateau borders where three films meet is also obtained.

General results for the shape of vertical films and of Plateau borders with gravity are also derived.

## 166.B2

## PATTERN FORMATION IN THIN FILMS

Ashutosh Sharma and R. Khanna

*Department of Chemical Engineering, Indian Institute of Technology, Kanpur-208016, India*

The free surface of a thin ( $< 100$  nm) fluid film becomes unstable and deforms spontaneously, whenever the disjoining pressure increases with an increase in the local film thickness. The problem of pattern selection, and the disjoining pressure-morphology relationship cannot be investigated by the linear stability theory. The nonlinear evolution of the instability, and the resulting 3-D patterns were investigated based on the numerical solutions of the full 2-D thin film equation. Results for two distinct types of thin films are presented: (I) films subjected to the long range van der Waals attraction and extremely short range Born repulsion. And (II) films subjected to the long range attraction combined with a shorter range repulsion. In the second case, the short range repulsion is derived from a thin wettable coating of the substrate, from acid-base interactions or from a weak adsorption of the polymer to the substrate.

In the first case, true dewetting occurs in the form of growing circular holes (Figure 1) which coalesce to form a giant polygonal structure eventually. The hole- radius grows as  $t^q$ , where the asymptotic value of the exponent  $q$  is about 0.87, which is in contrast to simplified analyses that predict  $q=1$ . The hole-rim was found to be asymmetric with substantially higher slopes near the three phase contact line. The dynamic contact angle during the hole growth was nearly constant, and could be approximated as  $0.8 \pm 0.05 \theta$ , where  $\theta$  is the equilibrium contact angle.

In the second case, true dewetting is suppressed, and the saturation of the initial instability leads to a quasi-stable bicontinuous structure reminiscent of the spinodal decomposition (Figure 2). This "morphologically phase separated" nonuniform interconnected structure consists of an array of micro-drops of varying shapes and sizes in quasi-equilibrium with largely flat thin films. The initial structure coarsens slowly by ripening and merger of drops due to spatial gradients of the Laplace and disjoining pressures. Both the short and the long range dynamics of the pattern evolution were quantified.

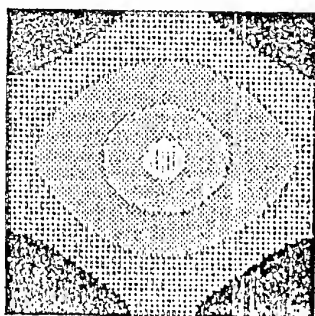


Figure 1

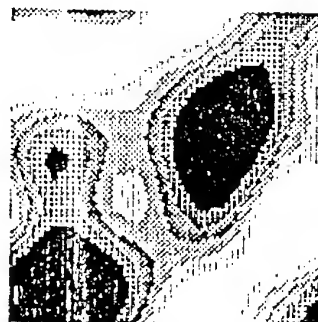


Figure 2

## 167.B2 THERMOCAPILLARY INSTABILITY IN A LAYER OF VARIABLE VISCOSITY LIQUID WITH A DEFORMABLE FREE SURFACE

S. G. Slavtchev<sup>1</sup>, P. G. Kalitzova-Kurteva<sup>1</sup>, I. A. Kurtev<sup>2</sup>

<sup>1</sup>*Institute of Mechanics, Sofia 1113, Bulgaria*

<sup>2</sup>*Technical University, Sofia 1156, Bulgaria*

Surface tension-driven flows are among the most interesting for their technological importance in many phase separation processes of chemical engineering and thermal processes of residual oil recovering by combustion. Spontaneous convection induced by surface-tension gradients due to mass or heat exchange through the interface between two phases is recognised as a significant factor for enhancing the transfer rates.

Marangoni instability in liquids has been studied not only for linear dependence of the surface tension on temperature (or concentration). The effects on the stability criteria of different factors, such as non-linear dependence of the surface tension on temperature, linear dependence of liquid viscosity on temperature, the non-Boussinesq approximation of the Navier-Stokes equations, etc., have been also considered. The aim of the present report is to show the influence of the exponential variation of the viscosity with temperature on the critical values of the Marangoni and wave numbers. Such a behaviour of fluid viscosity is registered for many oils.

The onset of stationary and oscillatory thermocapillary convection in a horizontal layer bounded from below by a rigid wall and open from above to the ambient motionless gas is studied by applying the linear stability analysis. The wall is considered either conducting or insulating to temperature disturbances. The free surface is assumed deformable. The eigenvalue problem is solved analytically and the corresponding solvability condition yields the critical Marangoni and wave numbers depending on the other characteristic parameters - Crispation, Prandil, Biot and Bond numbers.

In the conducting case, there exist two modes of stationary instability: short-scale mode, driven by surface-tension gradients, and long-scale mode, influenced by gravity and capillary forces, due to the free surface deformability. The variation of the viscosity influences mainly the short-scale mode instability threshold. In the insulating case, one mode can only occur and its wavelength is large when the free surface is thermally insulated or short if there is a heat transfer between the both phases.

The principle of exchange of instabilities is not valid for variable viscous fluids and high frequency oscillatory convection can appear in the layer.

## 168.B2 ELECTRICAL CONDUCTANCE OF THIN FOAM FILMS

E.N. Swayne, John Newman, and C.J. Radke

*Chemical Engineering Department, University of California, Berkeley, CA 94720 USA*

Elucidating the molecular structure of and thin film forces in isolated lamellae is fundamental to understanding foam stability. For the first time, we directly measure in the same apparatus disjoining pressures and electrical conductances of thin aqueous foam films stabilized by ionic surfactants as a function of film thickness. A novel porous-disk annular film holder permits electrical measurements in the direction parallel to the film while simultaneously allowing determination of the disjoining pressure isotherm. The film holder is a concentric ring-disk assembly constructed of porous stainless steel. The outer ring-disk and the inner disk serve as electrodes, and the film is formed in the annulus between the two porous disks. Equilibrium disjoining pressures are obtained from the known applied capillary pressures whereas film thicknesses follow from interferometry. The unique annular shape of the film forces current to flow radially through the film. To avoid electroosmosis AC electrical measurements are necessary. Measured film electrical currents and voltages vary strongly with frequency. Thus, to quantify the film conductances, we employ galvanostatic AC impedance spectroscopy and determine the real and imaginary parts of the impedance over a broad range of frequencies from 10Hz to over 65 kHz. Film resistance is found as the intercept in a complex-plane impedance diagram.

Disjoining pressure measurements of common black films for sodium dodecylsulfate in a dilute sodium nitrate aqueous electrolyte confirm available literature data. Preliminary film electrical conductance



data as a function of film thickness exhibit excess surface conductivities that properly scale with ionic strength and that show diminished ionic mobilities compared to those in the bulk. DLVO theory fitted to the measured disjoining pressure isotherms gives the charge density at the surface. Using this same charge density and diffuse double layer theory we correctly predict the observed trends in film resistance. Simultaneous determination of film electrical and force distance behaviour provides a new tool for understanding molecular architecture of thin films.

## 169.B2 DEWETTING: STABLE AND UNSTABLE GROWTH OF PORES

U. Thiele and W. Pompe

MPAG "Mechanik heterogener Festkörper at Dresden University of Technology, Hallwachsstr. 3, D-19069, Dresden, Germany

During drying of spin-coated films of aqueous solutions of monomeric collagen different morphologies caused by dewetting instabilities have been observed. These range from networklike to ramified structures depending on collagen concentration and wettability of the substrate [1]. It can be shown that the transition between both morphologies comes from an instability of the rim at the dewetting fronts.

For the case of a negative Hamaker constant  $A$  the profile of the dewetting front has been numerically calculated and compared with the  $A > 0$  case [2]. The profile near the contact line is discussed in detail. The moving rim of the dewetting front is unstable. The instability has been analyzed is shown in analogy to the work of Troian et al. [3] regarding gravitation driven flow of a fluid front.

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## 170.B2 SPREADING OF LIQUID CRYSTALS

M.P. Valignat, S. Bardon, A.M. Cazabat

Physique de la matière condensée, Collège de France, Paris, France

We present ellipsometric measurements of the thickness profiles of mesogenic compounds spreading on solid surfaces. From the shape and time evolution of the profiles, information about orientation of liquid molecules and interaction between these molecules and the solid surface can be obtained.

On bare silicon substrate nematic droplets may exhibit a "smectic-like" behavior close to the solid surface (two or three steps of around 30 Å spread out, depending on the relative humidity and on the temperature). In the thicker part of the drop a shoulder of thickness  $L_2$  (around 200 Å) appears in the profile. During spreading, the top of the drop becomes flatter, decreasing to the thickness  $L_2$  then breaks down to the "smectic-like" film. A simple model involving long and short range interaction is used to interpret this behavior. The smectic phase also wets the surface and a precursor film grows, which radius  $R$  scales like the square root of the time  $t$ :  $\Delta R = (Dt)^{1/2}$ . The diffusion coefficient  $D$  decreases with temperature and vanishes several degrees below the melting temperature, i.e., the solid phase also spreads out through a precursor film. The effect is analyzed in terms of surface induced remelting.

## 171.B2 EFFECT OF THE SURFACTANT CONCENTRATION ON THE KINETIC STABILITY OF THIN FOAM AND EMULSION FILMS

K. P. Velikov<sup>1</sup>, O. D. Velev<sup>1</sup>, K. G. Marinova<sup>1</sup> and G.N. Constantinides<sup>2</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, University of Sofia, Faculty of Chemistry, J. Bouchier Ave. 1, 1126 Sofia, Bulgaria.

<sup>2</sup>Department of Chemical Engineering, University of Patras, and Institute of Chemical Engineering and High Temperature Chemical Processes, GR 26500, Patras, Greece.

The thinning and the lifetime of aqueous foam and emulsion films formed in a model experimental cell were investigated [1]. The foam films were stabilised by either Sodium Dodecyl Sulphate or Sodium Dodecyl Polyoxyethylene-2 Sulphate. The emulsion films contained either Tween 20 or Span 20 which are typical nonionic stabilisers of industrially produced emulsions. Xylene was used as an oil phase. Tween 20 is water soluble and was dissolved in the aqueous phase. Span 20 is predominantly oil soluble and was dissolved in the xylene phase. To suppress the long-range electrostatic repulsion between the film surfaces 0.1 M NaCl presented in the water solutions.

We have defined and measured the hydrodynamic contribution to the film lifetime as the time elapsed from the film formation until the critical thickness is reached. The time of hydrodynamic drainage of the films increased linearly vs. the logarithm of the surfactant concentration. This linear dependence was valid despite of the type of the film, the type of the surfactant and not only below the Critical Micelle Concentration (CMC) but also much above this concentration threshold (up to 100 times CMC).

The experimental results are relevant to the hydrodynamic basis of foam and emulsion stabilisation. They are compared against the earlier hydrodynamic theories of film drainage. A reasonable, but not excellent agreement between the experimental data and the theory could be achieved in the region below the CMC of the surfactant. The data above the CMC still remain unexplained by an adequate theory. The investigation provides some guidelines for choosing the optimal type and concentration of surfactant in colloid systems of practical importance.

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## 172.B2 DIRECT OBSERVATION OF THE DYNAMICS OF LATEX PARTICLES CONFINED INSIDE THINNING WATER-AIR FILMS

K. P. Velikov and O. D. Velev\*

Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, University of Sofia, Faculty of Chemistry, J. Bouchier Ave. 1, 1126 Sofia, Bulgaria.

\*Present address: Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716-3110, USA

The dynamics of micrometer-size polystyrene latex particles confined in thinning foam films was investigated by microscopic interferometric observation [1]. The behaviour of the entrapped particles depends on the mobility of the film surfaces, the particle concentration, hydrophobicity, and rate of film formation. When the films were stabilised by sodium dodecyl sulphate no entrapment of particles between the surfaces was possible. When protein (BSA) was used as a stabiliser, a limited number of particles were caught inside the film area due to the decreased mobility of the interfaces. In this case, extraordinary long-ranged ( $> 100 \mu\text{m}$ ) attraction leads to two dimensional (2D) particle aggregation. A major change occurs, when the microspheres are partially hydrophobised by the presence of cationic surfactant (DTAB or HTAB). After the foam films are opened and closed a few times, a layer of particles simultaneously adsorbed to the two interfaces is formed, that sterically inhibits any further film opening and thinning. The particles within this layer show an excellent 2D hexagonal ordering. The experimental data are relevant to the dynamics of defects in coating films, Pickering emulsions and particle assembly into 2D arrays.

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## 173.B2

## BLACK EMULSION FILMS OF PROTEINS

G.P. Yampolskaya, S.M. Levachev, V.N. Izmailova

*Moscow State University, Moscow, Russia*

Thin films simulating o/w emulsions are poorly investigated in contrast to BLM. Water soluble globular proteins stabilize at determined conditions similar films. In many cases stable films of a large thickness (more than of black films one) are formed. The determination of conditions of the black emulsions films formation and physical chemical factors affecting on the film stability or rupture is objective of this work. The investigation was performed by means of the Sheludko-Exerova device.  $\alpha$ -chymotrypsin (Cht) and bovine serum albumin (BSA) were used as stabilizers. The varying of following parameters: protein concentrations in aqueous solutions, pH and temperatures allowed to determine a diagram, characterizing a thickness of stable films. Ultimate thin - black - films of Cht are formed in the narrow range of the protein concentration ( $6.6 \cdot 10^{-6} \div 1.6 \cdot 10^{-5} \text{ M}$ ), of pH ( $6.0 \div 7.2$ ) and temperatures ( $20 \div 30^\circ \text{C}$ ). The formation of thick films is connected with polymolecular adsorption of protein at interface (data of the radioactive indicators method using T-labelled proteins) and structure-rheological properties of interfacial adsorption layers (IAL). The flow character of IAL at the load with constant deformation velocity (in the range of  $4 \cdot 10^{-4} \div 4 \cdot 10^{-1} \text{ c}^{-1}$ ) allows to consider IAL as viscous-elastic liquids. These properties of IAL determine dimpling of films at large radius. Mechanism of the black film formation is discussed: the repeated many times jumpily film formation of smaller thickness in the stable initially thick film (this phenomenon is known for BLM); the LAL flow in the thinning processes and particles dispersing from IAL in the nonpolar phase.

The other factor affecting on the film stability is the addition in the system of lipids (lecithin). Small lipid additives in the organic phase ( $10^{-8} \div 10^{-7} \%$ ) cause the black film formation at smaller protein concentrations. Further increase in lipid concentration leads to the formation of grey films and then films became unstable. The black films stability is preserved up to ratio protein/lipid ([P/L]) 25: 1. At small lipid concentration rheological behavior of IAL are not changed but at the approaching of [P/L] to the critical value (for the film stability) viscous-elastic properties of IAL are disappeared. The lecithin addition causes changes of sizes of associated particles in both liquid phases. In aqueous phase the particles size is independent on [P/L], but in nonpolar phase large particles are formed at the small [P/L], when emulsion films are black and stable. Size of particles in organic phase drastically decreases in conditions corresponding to the film rupture. Interfacial tension decreases to the small values. ( $\sim 1 \text{ mN/m}$ ). The system acquires properties of micro-emulsions. Thermodynamic properties of the system affect as a factor of the film instability.

## 174.B2

## HYDROPHOBIC AND HYDRATION FORCES IN SOAP FILMS

Roe-Hoan Yoon and B. Suha Aksoy

*Center for Coal and Minerals Processing, Virginia Polytechnic Institute and State University,  
Blacksburg, Virginia 24061*

Equilibrium thicknesses of soap films were determined using the thin film balance (TFB) of Scheludko-type. The soap films were stabilized with dodecylammonium chloride (DAH) and sodium dodecylsulfate (SDS). The data were analyzed in view the extended DLVO theory, which considers electrostatic, van der Waals, and hydrophobic forces. The hydrophobic force was represented by a power law which is of the same form as for the van der Waals force, so that its constant K can be directly compared with the Hamaker constant, A. At low surfactant concentrations, the K values are positive, indicating the presence of hydrophobic forces in soap films. As the concentration increases, K decreases, suggesting that the ionic surfactants dampen the hydrophobic force. At concentrations above  $2 \times 10^{-3} \text{ M}$  for DAH and  $1.3 \times 10^{-3} \text{ M}$  SDS, K becomes negative most probably due to the appearance of hydration force. Plots of the positive K values obtained with both the cationic and anionic surfactants fall on the same curve.

The TFB was also used for obtaining disjoining pressure isotherms at  $10^{-3} \text{ M}$  DAH (in the presence of  $10^{-4} \text{ M}$  NaCl) and  $10^{-4} \text{ M}$  SDS (in the presence of  $4 \times 10^{-4} \text{ M}$  NaCl). The results can be fitted to the extended DLVO theory with  $K = 6 \times 10^{-19} \text{ J}$  for DAH and with  $K = 5.5 \times 10^{-19} \text{ J}$  for SDS. Consideration of

hydrophobic force predicted rupture thicknesses larger than predicted using the DLVO theory, but are substantially smaller than the experimental values. This discrepancy may be ascribed to the hydrodynamic force operating in the film thinning process.

## 175.B3

### HUMIDITY EFFECTS ON THE MESOPORES OF HARDENED CEMENT PASTE

Jürgen Adolphs, Max Josef Setzer

*Universität Gesamthochschule Essen, Germany*

From investigations of the dynamic elastic modulus [1] and of SAX (small angle X-ray) [2] from hardened cement paste (hcp) it is well known that non-linear humidity dependent changes of the specific surface areas and elastic properties occur. Mercury intrusion porosimetry and Nitrogen adsorption are used to measure the humidity influence on the pore size distribution and the specific surface area. Special techniques of preparation are necessary. The results show a distinct but also divergent shift of the mesopore radii. During a storage of the hcp samples until 50% rh. an increase of the mesopore radii is observed. In the upper humidity region above 50% rh. a decrease is detected. A similar tendency is observed for the specific surface areas and the sorption energies calculated with the ESW-Method [3, 4]. The results are correlated with data of the dynamic elastic modulus, SAX, water vapour diffusion, length change, carbonation and other mechanical properties. The divergence behaviour can be interpreted by two physical processes. The change of the surface tension by adsorbed water layers seems to be the major effect in the lower humidity region. The second effect for the upper humidity range is the disjoining pressure, inducing an increase of the sample density. With the proposed connection of the adsorption model ESW [3, 4] and the disjoining pressure model by Churaev [5] it will be possible to calculate this phenomenon.

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## 176.B3

### DIHEDRAL ANGLES OF LENS AND INTERFACIAL TENSION OF AIR/LONG CHAIN ALCOHOL/WATER SYSTEMS

Makoto Aratono<sup>1</sup>, Takayuki Toyomasu<sup>1</sup>, Takeo Shinoda<sup>1</sup>, Norihiro Ikeda<sup>2</sup> and Takanori Takiue<sup>1</sup>

<sup>1</sup>*Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812-81, Japan*

<sup>2</sup>*Faculty of Human Environmental Science, Fukuoka Women's University, Fukuoka 813, Japan*

The dihedral angle of an alcohol lens at the air/water interface and the three kinds of interfacial tensions of air/long chain alcohols/water systems have been measured by the newly constructed apparatus as a function of temperature from 288.15 to 313.15K at 2.5K intervals under atmospheric pressure. The alcohols used were 1-octanol (C<sub>8</sub>OH), 1-decanol (C<sub>10</sub>OH), 1-undecanol (C<sub>11</sub>OH), and 1-dodecanol (C<sub>12</sub>OH). By comparing the dihedral angles measured with those calculated by applying Neuman relations to the interfacial tension values, it was concluded that the dihedral angle measurement was performed with a satisfactory accuracy. The properties of the interfacial film and also the occurrence of the intruding of water phase on the air/alcohol interface were discussed.

*Interfacial Tension:* The air/water ( $\gamma_{AW}$ ), air/alcohol ( $\gamma_{AO}$ ), and alcohol/water ( $\gamma_{OW}$ ) interfacial tensions were measured as a function of temperature by pendant drop method. The  $\gamma_{AO}$  values decrease smoothly with increasing temperature. All the  $\gamma_{AW}$  vs T curve have a positive slope and only the one of C<sub>11</sub>OH has a break point at which the slope changes abruptly. All the  $\gamma_{OW}$  vs T curve have also a positive

slope and the curves of  $C_{11}OH$  and  $C_{12}OH$  have a break point. The thermodynamic analysis of the data shows that the phase transition of the interfacial film takes place between the expanded and condensed state at the air/water interface of  $C_{11}OH$  and the alcohol/water interfaces of  $C_{11}OH$  and  $C_{12}OH$ .

*Dihedral Angles:* The dihedral angle  $\theta_0$  interposing the alcohol lens was evaluated by summing the two angles: the angle between the air/alcohol interface and the plane containing the three-phase contact line  $\theta_0$  and that between the alcohol/water interface and the contactline  $\theta_L$ . The  $\theta$  values depend only slightly both on temperature and the chain length. On the other hand, the  $\theta_L$  value decreases with increasing temperature and decreasing the chain length. It was found that the  $\theta_L$  vs  $T$ , and therefore the  $\theta_0$  vs  $T$ , curve has break points at the phase transition temperatures.

*Interfacial Tension and Dihedral Angles:* The wetting-nonwetting transition, the intruding phenomena of the water phase into the alcohol/water interface, and their relation to the state of interfacial films were discussed based on the results of the interfacial tensions and dihedral angles.

## 177.B3

### SURFACE (2-D) ELECTROSTATICS AND ITS ROLE IN THE NEW-PHASE FORMATION AT LIQUID-GAS INTERFACE

M. Avramov, B. Radoev and K. Dimitrov

*University of Sofia, Department of Physical Chemistry, 1126 Sofia, Bulgaria*

By analogy to the strong effect of electric charges on new-phase formation in bulk (barrier-less condensation upon electrically charged free droplets), similar effects have been sought at liquid-gas interfaces. A specific feature of the analysis in the latter cases is that electrostatic problems in complex "bulk+heterogeneous surfaces" spaces must be considered. As far as electrostatic fields propagate differently in 2-D and in 3-D spaces, non-trivial generalizations of the classical (3-D) case are to be expected. Special non-conventional methods are needed for solution of such electrostatic problems as well (the so called mixed boundary value problem).

In the present investigation some "pure" two-dimensional systems, typical for heterogeneous monolayers, are analyzed as a preliminary step to the general solution:

- A single uniformly/non-uniformly charged circle situated in neutral/charged (with electrical double layer) dielectric medium;
- A surface lattice of charged circles interacting via 2-D Debye atmospheres.

The results from the analysis are applied to the thermodynamic treatment of nucleation and the contribution of electrostatics to the equilibrium size and concentration of the nuclei is evaluated.

## 178.B3

### GRAZING INCIDENCE X-RAY DIFFRACTION WITH IMAGING PLATE DETECTION FOR INVESTIGATING THE STRUCTURES OF LANGMUIR-BLODGETT FILMS

G.T. Barnes<sup>1</sup>, I.R. Gentle<sup>1</sup>, J.B. Peng<sup>1</sup>, and G.J. Foran<sup>2</sup>

<sup>1</sup>*Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia,*

<sup>2</sup>*Australian Nuclear Science and Technology Organization, PMB 1, Menai, NSW 2234, Australia*

Grazing incidence X-ray diffraction has been used for some years to investigate the structures of Langmuir-Blodgett (LB) films but the usual detection technique of scanning with a position sensitive detector does not usually reveal the full complexity of the diffraction pattern. Moreover, the scanning process is very slow (taking typically 30 to 100min). With imaging plate detection the complete pattern from zero to high azimuthal angles can be obtained in the one exposure with exposure times from 20 s to 200 s. With a camera that holds several imaging plates a series of exposures can be made with the one sample without opening the vacuum chamber in which the measurements are made.

Two examples will be presented and discussed.

- LB films of cadmium behenate with 1, 3, and 5 layers are compared. The single monolayer has an hexagonal in-plane structure with short-range positional order and no off-plane features. With 3 layers there is no trace of the monolayer structure: instead there is the pattern of a centered monoclinic structure with a layer structure arising from the acyl chains. With 5 layers the pattern for the 3-layer film is seen with the addition of a layer structure arising from the layers of cadmium ions.
- LB films of cadmium arachidate (31 layers) at temperatures below 90 °C have a centered rectangular in-plane structure with vertical acyl chains. At about 105°C an intermediate structure is also seen. At 107 °C the layer structures are entirely replaced by a two-dimensional columnar structure. The transitions are slow and their kinetics have been followed by successive exposures with the X-ray camera.

## 179.B3

### PATTERN FORMATION IN COLLOIDAL MONOLAYERS

J.C. Earnshaw and F. Ghezzi

*The Department of Pure and Applied Physics, The Queen's University of Belfast,  
Belfast BT7 1NN, Northern Ireland*

Colloidal particles trapped at a liquid/air interface provide a model system to study matter in two dimensions. The main advantage of such studies is the ease of visualization of the structures formed. The particle-particle interactions in the system can be varied experimentally. Under certain conditions cluster-cluster aggregation occurs, leading to fractal structures [1]. However, using a range of different experimental conditions we have found that it is possible to induce the formation of a variety of different structures. For example, clustering may involve the appearance of small, highly ordered arrays of particles. Again, under different conditions the particles tend to aggregate into long linear structures. These lines tend to lie parallel to each other, and can collapse towards each other, forming rather regularly-sized loops. Various experiments suggest that such different behaviours reflect competition between the different forces acting upon the particles, electrostatic and capillary in nature. The mechanisms underlying these novel observations will be discussed.

1. D.J. Robinson and J.C. Earnshaw, Phys. Rev. A, 46, 2045,32055, 2065 (1992).

## 180.B3

### CORRELATION BETWEEN MONOLAYER STRUCTURE AND SURFACE PROPERTIES OF ALKYL DIMETHYL PHOSPHINE OXIDES UNDER DYNAMIC CONDITIONS. BAM STUDIES

D.O. Grigoriev<sup>1,2</sup>, G. Kretzschmar<sup>1</sup>, J.B. Li<sup>3</sup>, B.A. Noskov<sup>2</sup> and R. Miller<sup>1</sup>

<sup>1</sup>MPI of Colloids and Interfaces, Rudower Chaussee 5, D-12489 Berlin, Germany

<sup>2</sup>Institute of Chemistry, St. Petersburg State University, Universitetskii pr. 2, 198904 St. Petersburg,  
Petrodvoretz, Russia

<sup>3</sup>International Joint Lab between Institute of Photographic Chemistry and MPI of Colloids and Interfaces,  
Chinese Academy of Sciences, Beijing 100101, China

A conventional LB trough - measurement of pressure-area-isotherms (P-A) - does not allow studies of the dynamics of structure changes and other processes happening during the compression or expansion of insoluble monolayers. The Brewster Angle Microscopy (BAM) is able to visualise the dynamics of monolayers and is therefore a very valuable supplement to the classical methodology. In the present paper both methods are used for the study of monolayers of the non-ionic surfactants alkyl dimethyl phosphine oxide, Eikosyl Dimethyl Phosphine Oxide (EDPO) and Octadecyl Dimethyl Phosphine Oxide (ODPO). The monolayers were spread from benzene, hexane or chloroform at  $c = 10^{-3}$  M on an aqueous subphase. The instrument used comprises a Langmuir trough equipped with an oscillating barrier. The BAM is mounted on the LB trough such that it can move synchronised with either the compressing/expanding or oscillating barrier. A special software is designed to adjust the BAM movement with respect to amplitude and phase shift of an oscillation.

The two homologues show significantly different monolayer behaviour although the alkyl chain of EDPO and ODPO differ by only two  $-\text{CH}_2-$  groups. While EDPO forms well visible domains, ODPO does not form any domains. For EDPO the domain formation starts at the kink point in the P-A isotherm. The BAM images of domain growth also correlate with the shape of the P-A isotherm. The absence of any domains in the ODPO monolayer is in line with its P-A isotherm showing no peculiarity up to the collapse pressure. A possible reason for the difference in the monolayer behaviour of the two homologues and the effect of the spreading solvent will be discussed. The results are compared also with data from literature.

A second group of experiments is dedicated to the study of the relaxation processes connected with the existence of domains and the determination of the viscoelasticity of the monolayers. A comparison of the viscoelasticity of EDPO (forms domains) with that of ODPO (does not show structures) allows to discuss the contribution of domains to the non-equilibrium monolayer behaviour. A relationship between monolayer structure and viscoelasticity is discussed.

### 181.B3 INFLUENCE OF THE CO-ION IN THE SUBPHASE ON THE STRUCTURE AND PROPERTIES OF THE MONOLAYERS FROM DPPG (DPPC)/NaCl + WATER

D. Grigoriev<sup>1,2</sup>, R. Krustev<sup>1,3</sup>, B. Radoev<sup>3</sup> and R. Miller<sup>1</sup>

<sup>1</sup>MPI for Colloids and Interfaces, D-12489 Berlin, Germany

<sup>2</sup>Institute of Chemistry, St.Petersburg State University, Petrodvoretz, Russia

<sup>3</sup>Department of the Physical Chemistry, University of Sofia, 1126 Sofia, Bulgaria

Two dimensional phase transition in Langmuir monolayers is one of the most interesting and important phenomena in such systems. The use of modern optical methods (Brewster Angle Microscopy (BAM) in the first place) combined with classical p/A measurements contributed substantially to the progress in the last decade of the in situ study of these processes. It was shown, for instance, that the new phase not only appears in a dispersed form but actually remained in such a state up to the point of collapse.

DPPG (DPPC) monolayers were used as a model system to study the role of Na co-ion on the liquid/gel phase transition: kinetics of growth, evolution of the shape of domains, etc. The surface charge was varied by varying the bulk concentration of NaCl from 0.001 to 0.5 M (via surfactant (DPPG) dissociation and direct adsorption of NaCl ions in the monolayers, resp.) The process was directly video recorded and subsequently treated by a standard frame grabber technique. Observation show that ionic strength has a significant effect on the kinetics of nucleation and the growth of domains. A characteristic feature of the domains is their shape with a distinct dendrite-like contour. The size of their loops diminish upon increasing pressure and ionic strength. A frame grabber treatment of the recorded material is used to obtain the size and concentration of domains as a function of time. The kinetic dependencies obtained are considered from the view point of the theory of crystallisation from melts.

### 182.B3 CHARACTERIZATION OF ACTIVE SITES FOR $\text{N}_2$ AND NO ADSORPTION ON COPPER-ION-EXCHANGED ZEOLITE (CuZSM-5)

Ryotaro Kumashiro<sup>1</sup>, Takefumi Yoshimoto<sup>1</sup>, Yasushige Kuroda<sup>2</sup> and Mahiko Nagao<sup>1</sup>

<sup>1</sup>Research Laboratory for Surface Science

<sup>2</sup>Department of Chemistry, Faculty of Science, Okayama University, Tsushima-naka, Okayama 700, Japan

It has been suggested that the monovalent copper-ion species ( $\text{Cu}^+$ ) formed by heat treatment *in vacuo* of the copper-ion exchanged ZSM-5 zeolite (CuZSM-5) which has an excess amount of copper ions in regard to a stoichiometry exhibits a high activity for the adsorption and decomposition of  $\text{NO}_x$ <sup>1</sup>. It was also revealed that this species strongly interacts with  $\text{N}_2$  molecules even at room temperatures<sup>2</sup>. The state of copper-ion species in CuZSM-5, however, is still obscured. In the present study, we intended to characterize the active sites for  $\text{N}_2$  and NO adsorption on the CuZSM-5 samples using carbon monoxide (CO) as a probe molecule.

The original ZSM-5 (Na-type, Si/Al = 11.9) sample was ion-exchanged at 363 K for several times using a  $\text{CuCl}_2$  solution ( $0.3 \text{ mol dm}^{-3}$ ) to obtain the copper-ion exchanged samples with different amounts of

copper ions<sup>2</sup>. The heats of adsorption and adsorption isotherms of CO and N<sub>2</sub> were determined at 301 K for the CuZSM-5 sample by using adsorption calorimeter. The infrared spectra of adsorbed species were recorded in the usual way.

Figure 1 shows the IR spectra for the CuZSM-5 sample taken after various treatments involving CO, N<sub>2</sub> and NO adsorption. Two absorption bands at 2159 and 2151 cm<sup>-1</sup>, which are obviously due to the CO species adsorbed irreversibly on the two types of Cu<sup>+</sup> species, are remained after evacuating the sample at room temperature (spectrum a). These bands were not affected by N<sub>2</sub> dosing to the sample. By the succeeding evacuation at 473 K, the lower-frequency band (2151 cm<sup>-1</sup>) disappeared. Re-dosing of N<sub>2</sub> gas to the same sample, in which one type of Cu<sup>+</sup> species was masked with strongly adsorbed CO molecule, gives a new band at 2295 cm<sup>-1</sup> ascribable to the physisorbed N<sub>2</sub> molecules, keeping the 2159 cm<sup>-1</sup>-band unchanged (spectrum b). All these bands disappeared after evacuation at 573 K. The differential heats of adsorption of N<sub>2</sub> on CuZSM-5 sample suggested the occurrence of at least two types of adsorption differing in interaction energy. When NO gas is introduced to the sample pretreated at 873 K, two absorption bands appear at 2295 and 1812 cm<sup>-1</sup>, which can be attributed to the adsorbed N<sub>2</sub> species (produced by decomposition of NO) on one type of Cu<sup>+</sup> species and to the NO species adsorbed on another type of Cu<sup>+</sup> species, respectively (spectrum c). However, the former band can not be observed for the sample evacuated at 473 K after CO adsorption and hence in which one type of Cu<sup>+</sup> species (responsible for 2159 cm<sup>-1</sup> band) being masked with strongly adsorbed CO molecule (spectrum d). From these results it may be concluded that at least two types of Cu<sup>+</sup> species are formed in the CuZSM-5 sample by heat treatment at higher temperature, and they act as active sites for N<sub>2</sub> and NO adsorption in such a manner as that the Cu<sup>+</sup> species which can interact weakly with CO act as effective sites for N<sub>2</sub> adsorption while the ones which can interact strongly with CO act as effective sites for NO adsorption.

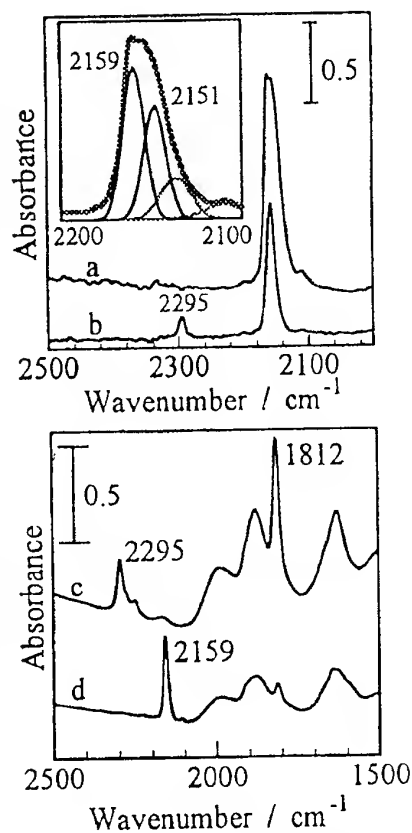


Fig.1. IR spectra of CuZSM-5. Inserted figure shows a deconvolution of spectrum a

1. M. Iwamoto, H. Yahiro, K. Tanda, N. Mizuno, Y. Mine and S. Kagawa, *J. Phys. Chem.*, 1991, 95, 3727.
2. R. Kumashiro, Y. Kuroda and M. Nagao, 14th IUPAC Conf. on Chem. Thermodyn., Osaka, 1996, p.232.

## 183.B3

### SURFACE CHEMISTRY AND SPECTROSCOPY OF THE 2D SOL-GEL PROCESS

Roger M. Leblanc, Frederic Facca and Germain Puccetti

*Department of Chemistry, University of Miami, Coral Gables, Florida 33124, U.S.A.*

The present study focuses upon the synthesis of nanometer scale oxide-based titanium films according to a two-dimensional sol-gel process at the air/liquid interface. First, surface pressure-area isotherms of the tetrabutoxy titanium were measured at  $22.0 \pm 0.5^\circ\text{C}$  on various subphases: pure water (pH=5.5), aqueous acetylacetone (0.01 M, pH=4.6), aqueous acetic acid (0.01 M, pH=3.3) and glycerol. At the same time, UV-vis absorption spectra were directly registered at the interface at different surface pressures. Then, we used a Brewster angle microscope to observe the film on different subphases. The results are interpreted as the formation of a macroscopic network of oxide bridges between titanium atoms over the pure water subphase. On the aqueous acetic acid and the glycerol subphases, the film is more complex and connected, involving two networks made of oxide and ligand bridges. In the case of the aqueous acetylacetone subphase, the resulting film is particularly dynamic and much less connected.



## 184.B3

INTERACTIONS OF WATER AND ALCOHOLS  
WITH ZIRCONIA SURFACEMahiko Nagao<sup>1</sup>, Koji Hiramatsu<sup>1</sup>, Koji Hirata<sup>1</sup> and Yasushige Kuroda<sup>2</sup><sup>1</sup>Research Laboratory for Surface Science<sup>2</sup>Department of Chemistry, Faculty of Science, Okayama University, Tsushima-naka, Okayama 700, Japan

Zirconia ( $\text{ZrO}_2$ ) is an important ceramic material and is also used widely as a refractory or a catalyst. Most of the researches on zirconia have been devoted to the bulk character rather than to the surface properties. Water exists everywhere on the earth, and hence the surface of solid, especially, the powder surface, stored in the atmosphere is covered with chemisorbed water (i.e., surface hydroxyl groups) which can play an important role in the chemical reaction taking place on the solid surface. Furthermore, the adsorption of organic substances on the solid surface is a fundamental phenomenon in understanding both catalytic process and surface modification.

In the present study, we have investigated the adsorption properties of zirconia surface by measuring the heats of immersion and adsorption isotherms of water, methanol and ethanol. Fourier infrared spectroscopy for adsorbed species was also applied.

The zirconia sample was first pretreated at 873 K and then exposed to the saturated water vapour to promote a complete surface hydroxylation, followed by evacuation at various temperatures from 298 to 873 K to obtain the samples with a controlled number of hydroxyls. For these samples the heats of immersion, adsorption isotherms and IR spectra of water, methanol and ethanol were measured.

The heat of immersion of zirconia into water increased with increasing evacuation temperature of the sample and gave a maximum value for the 873 K-treated sample. The same tendency as for water was obtained for both methanol and ethanol, though the heat-of-immersion value at the same temperature was smaller in the order, water > methanol > ethanol.

The differential heat of adsorption of water obtained from the data of heat of immersion and adsorption amount decreased with increasing coverages in the initial part, and succeedingly gave a constant value of  $134 \text{ kJ} \cdot \text{mol}^{-1}$  (which can be regarded as an average heat of hydroxylation of surface,  $Q_{\text{hyd}}$ ) in the wide adsorption range between 0.03 and  $0.10 \text{ cm}^3 \cdot \text{m}^{-2}$ . Corresponding to this adsorption region the IR data of adsorbed species showed that the dissociative adsorption of water takes place on the samples treated at higher temperatures. The presence of plateau in the heat curve indicates the existence of a homogeneous surface on zirconia.

As for the adsorption process of alcohol on metal oxide, two possible mechanisms will be expected for chemisorption: a dissociative adsorption on the bare surface and an esterification reaction with surface hydroxyl groups. On the basis of these experimental data, we found that both types of absorptions occur on the zirconia surface depending upon the content of surface hydroxyls. The heat of dissociative adsorption ( $Q_{\text{dis}}$ ) should give a maximum value for the 873K-treated sample on which the hydroxyl content is practically zero, while the heat evolved by the esterification reaction ( $Q_{\text{est}}$ ) should be maximum for the 298 K-treated sample which has a maximum hydroxyl content. If we assume that these two reactions occur simultaneously on the surface with intermediate hydroxyl contents and that the additivity of these two types of heats is established, a linear relationship would be obtained between the heat-of-immersion value and the hydroxyl content of the sample. By analysis of the present experimental data, we obtained a good linear relationship, and estimated the values of  $Q_{\text{dis}}$  and  $Q_{\text{est}}$  to be  $175$  and  $36.5 \text{ kJ} \cdot \text{mol}^{-1}$  respectively, in the case of methanol adsorption. The difference between them,  $139 \text{ kJ} \cdot \text{mol}^{-1}$ , should correspond to the heat of hydroxylation of the surface. The heat-of-adsorption value for water obtained above ( $Q_{\text{hyd}}$ ) is close to this value. For ethanol adsorption, the same value as for methanol was obtained;  $Q_{\text{hyd}} = 140 \text{ kJ} \cdot \text{mol}^{-1}$ . Other values were  $Q_{\text{dis}} = 156 \text{ kJ} \cdot \text{mol}^{-1}$  and  $Q_{\text{est}} = 16.5 \text{ kJ} \cdot \text{mol}^{-1}$ .

The IR spectra showed a new OH band when alcohol was adsorbed on the zirconia pretreated at higher temperatures, supporting the concept of dissociative adsorption of alcohol on such surface.

## 185.B3

## POINT DEFECTS IN LB FILMS OF Cd ARACHIDATE

George Nechev<sup>1</sup>, Masahiro Hibino<sup>2</sup>, Ichiro Hatta<sup>2</sup><sup>1</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Block 21,  
1113 Sofia, Bulgaria*<sup>2</sup>*Department of Applied Physics, Nagoya University, Nagoya 464-01, Japan*

One of the numerous potential application of Langmuir-Blodgett (LB) films in surface science is that they can be considered as model systems for the study of some typical phenomena of physics in two dimensions. Previous studies on LB films with atomic force microscopy (AFM) show that they possess characteristics that are typical for two-dimensional solids, following the prediction of Kosterlitz-Thouless-Halperin-Nelson-Young theory. According to the theory point defects play a major role in the melting of a two dimensional solid. AFM provides new opportunities to observe clearly the organisation and structure of such topological defects.

True molecular resolution with the atomic force microscope has been achieved, on Langmuir-Blodgett multilayers, using films of cadmium arachidate on mica. The images were obtained with 12  $\mu\text{m}$  scanner head and commercially purchased cantilevers with spring constant  $k=0.06 \text{ Nm}^{-1}$  under ambient conditions. The presence of vacancies in the LB film was shown for the first time and is the evidence that AFM is a true probe for imaging molecular structure of soft organic materials. Well-preserved raw image of an isolated dislocation from one side and absence of a hexatic order in the three layers LB film of Cd Arachidate from the other side show that LB films occupied an intermediate place between 2D and 3D dimensional solids. The probability for existence of vacancies and free dislocations is discussed in the light of KTHNY theory.

## 186.B3

CONFORMATION OF POLYSILOXANE IN MONOLAYERS  
ON LIQUID SURFACES

V.A. Ogarev

*Institute of Physical Chemistry, Russian Academy of Sciences, Lenin Prospect 31, 117915 Moscow, Russia*

The molecule conformation of flexible linear polysiloxane in insoluble monolayers on liquid surfaces has been examined. All monolayers exhibit reversible behaviour during compression-expansion cycles, monolayers are formed from bulk phase spontaneously. It allows to consider the monolayer similar to two-dimensional equilibrium solution.

Analysis of the surface pressure isotherms, surface potential, static elasticity, surface viscosity led to the conclusion that macromolecules form on a liquid surfaces two-dimensional random coil from flat oriented or undulate structure of chain. The criteria for these structures of chain is surface energy of subphase.

The region of dilute monolayer is described well by two-dimensional analogues of Want-Goff equation. In the region of concentrated two-dimensional solution the scaling critical exponent for the radius of gyration of the polymer chain indicate that liquids are theta solvents in surface layers.

Collapse monolayers during compression is realized by successive destruction of macromolecule structures which are peculiar for each Subphase. This process is accompanied by increasing of freedom degree of chain and promote the formation of the spiral macromolecule conformation inherent in the bulk polymer.

Finally, the structure of polysiloxane molecules on liquid surfaces can change both in the frame of two-dimensional statistical coil-flat oriented or undulate - which depends on the surface energy of subphase and under collapse of veritable monolayer. Collapse monolayer is fixed as a first-order phase transition. The more reduction of two-dimensional chain restriction the more phase change expand in monolayer.

### 187. B3 INTERFACIAL DIELECTRIC CONSTANT OF LANGMUIR MONOLAYERS OF MONO-, DI- AND TRIGLYCERIDES - EFFECT OF DIFFERENT HYDRATION OF THE HYDROPHILIC HEADS

Jordan G. Petrov, Anton Dafinov and George Nechev

*Institute of Biophysics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Block 21,  
1113 Sofia, Bulgaria*

Electrostatic characteristics of membranes are important for transmembrane transport and adsorption of proteins and other biologically active molecules on them. Langmuir monolayers at the air-water interface can serve as appropriate models that closely resemble the structure and packing of membrane lipids. Their chemical character and density govern the orientation of the polar heads and water structure at the interface and determine the interfacial dipole potential and local dielectric permeability. These magnitudes can be evaluated via measuring the shift of dissociation constant of an acid-base lipid pH-indicator embedded in the monolayer, with respect to the corresponding water bulk value.

We have determined  $\Delta pK$  of 4-heptadecyl-7-hydroxy coumarin and the interfacial dielectric constant for three lipid monolayers with systematically decreasing hydration of the hydrophilic heads - glycerol-1-monopalmitat, glycerol-1,2-dipalmitat and glycerol tripalmitat. The effect of decreasing number of hydroxyls on the hydration of the hydrophilic head was studied. It was shown that all three monolayers considered have practically the same polarity and dielectric constant which, however, significantly differs from the much higher value of bulk water.

### 188. B3 LANGMUIR MONOLAYERS WITH $CF_3$ GROUPS IN THE HYDROPHILIC HEADS - EFFECT ON THE INTERFACIAL DIPOLE POTENTIAL AND RELATED PHENOMENA

Jordan G. Petrov<sup>1</sup> and Helmuth Möhwald<sup>2</sup>

<sup>1</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Block 21,  
1113 Sofia, Bulgaria*

<sup>2</sup>*Max-Planck Institute of Colloids and Interfaces, Rudower Chaussee 5, 12489 Berlin, Germany*

Interfacial dipole potential and structure of hydration water of biomembranes are responsible for selective binding and permeability rates of ions, their short range interactions, etc. Langmuir monolayers of ethyl and trifluoroethyl esters of behenic acid at the air-water interface are considered as models of neutral biointerfaces with significantly different electrostatic properties. The effect of the replacement of the  $CH_3$  terminal of the ester radical by a  $CF_3$  group possessing an opposite dipole moment and different affinity towards water are studied. The following interfacial properties and phenomena are addressed:

Interfacial potential and dipole moment of neutral monolayers and contribution of the hydrocarbon chains, hydrophilic heads and hydration water to them.

Adsorption and penetration of ions at the monolayer caused by the dielectric inhomogeneity in the head group and hydration water regions.

Mechanical stability of the spread monolayers and formation of specific "heads-to-tails" multilayer structures at the air-water interface after monolayer collapse.

It was found that trifluoroethyl and ethyl behenate monolayers exhibited opposite surface potentials and dipole moments. This result demonstrates the predominant contribution of the hydrophilic heads to the surface dipole potential and dipole moment of the monolayers studied.

The effects of pH and ionic strength of the aqueous subsolution were shown to be insignificant. However, subsolutions containing 0.1 M KSCN cause a small but meaningful changes of  $\Delta V$  which could be due to a breaking of the structure of hydration water by the haotropic  $SCN^-$  anion or could result from specific adsorption of  $SCN^-$  at the polar head groups.

An increase of the absolute value of  $\Delta V$  after the collapse was observed for the fluorinated monolayers; the corresponding ethyl ester shows a decrease of  $\Delta V$  during the monolayer collapse. This

unusual behaviour is a new independent confirmation of the formation of "heads-to-tails" multilayers at the air-water interface observed first by Lundquist in the early 70'es.

**189.B3****DYNAMICS OF LANGMUIR-BLODGETT DEPOSITION:  
A MOLECULAR-HYDRODYNAMIC DESCRIPTION**

**Peter G. Petrov and Jordan G. Petrov**

*Bulgarian Academy of Sciences, Institute of Biophysics, Acad. G. Bonchev St., Block 21,  
1113 Sofia, Bulgaria*

The process of Langmuir-Blodgett deposition is described from the viewpoint of dewetting dynamics. The theoretical analysis takes into account two basic sets of interactions during the deposition process: (i) adsorption interactions between the head groups of the monolayer molecules, and (ii) viscous friction in dynamic meniscus near the three-phase contact line. Theoretical dependences of the *quasistatic* and *extrapolated* dynamic contact angles on contact line velocity are found. Comparison with the available experimental data shows a fairly good coincidence between the proposed molecular-hydrodynamic model and the experiment. The analysis of the energy dissipated during the deposition shows that the adsorption interactions are mainly responsible for the deposition dynamics. Viscous dissipation in the receding meniscus becomes important only at small dynamic contact angles, *i.e.* when the contact line velocity approaches the critical velocity of liquid film entrainment.

**190.B3****MODELLING OF ORIENTATIONAL TRANSITIONS  
IN MONOLAYERS OF AMPHIPHILIC MOLECULES**

**H. Schlacken<sup>1</sup>, P. Schiller<sup>1</sup>, O. Seidel<sup>2</sup>, H.-J. Mögel<sup>2</sup>**

*<sup>1</sup>Martin Luther University Halle-Wittenberg, Institute of Physical Chemistry, Mühlpforte I,  
D-06108 Halle, Germany*

*<sup>2</sup>Freiberg University of Mining and Technology Institute of Physical Chemistry,  
D-09596, Freiberg, Germany*

It is well known that monolayers of amphiphiles are important in colloids, detergents and biological membranes. Adsorbed amphiphilic molecules form monolayers at the interface between water and air. The amphiphiles of Langmuir monolayers are only slightly soluble. The hydrophilic heads of the molecules are grafted on the interface, while the hydrophobic hydrocarbon tails remain out of water. These monolayers form a rich variety of two dimensional phases including fluid, hexatic and crystalline states. The isotherms of pressure-area diagrams show horizontal sections and deflection points indicating first order and second order phase transitions. In most ordered phases the long molecules are tilted towards the substrate plane. Some phase transitions of Langmuir monolayers are accompanied with an alteration of the tilt order.

Well-established statistical theories for three-dimensional liquid crystals favour the supposition that molecular repulsive interactions are sufficient to explain the parallel alignment of long molecules in the liquid crystalline nematic phase. Using a similar concept, we consider an ensemble of tilted rod-like particles grafted on a surface. The "scaled particle theory" applied to this system leads to a free energy functional which depends on the orientational distribution of the particle axes. For low surface densities the isotropic distribution is found to be always stable. If the density exceeds a critical value the particle align cooperatively. Apart of the isotropic state the model predicts the occurrence of two differently ordered phases, which are stable at higher densities. Phase diagrams are found to be strongly dependent on the geometry and the tilt angle of the grafted particles. In most cases the phasetransitions are predicted to be second order.

Conclusions of the molecular statistical model can be compared with results obtained from the experimental investigation of Langmuir monolayers. Taking into account discrete distributions for the particle orientation, our model is also applicable to phase transitions of long particles adsorbed on a crystalline substrate.

## 191.B3

MIXED MONOLAYER PROPERTIES OF TETRADECANOIC  
ACID WITH *n*-PERFLUOROCARBOXYLIC ACIDS  
WITH 10, 12, 14, 16, AND 18 CARBON ATOMS

Osamu Shibata<sup>1</sup>, Shigekazu K. Yamamoto<sup>2</sup>, Sannamu Lee<sup>2</sup>, Gohsuke Sugihara<sup>2</sup>

<sup>1</sup>Department of Pharmaceutical Technology, Faculty of Pharmaceutical Sciences, Kyushu University,  
Maidashi, Higashi-ku, Fukuoka 812-82, Japan

<sup>2</sup>Department of Chemistry, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-80, Japan.

It has been well known that fluorocarbon chain and hydrocarbon chain cannot mix well each other in a three dimensional matrix due to a large difference in cohesive force between them. For example, sodium perfluorooctanoate as a fluorocarbon surfactant and sodium decylsulfate as a hydrocarbon one cannot form a mixed micelle but form separate micelles of the respective components. However, if the interaction between head groups is sufficiently strong, hydrocarbon and fluorocarbon surfactants, e.g., the combination of sodium perfluorooctanoate with MEGA-9, are well miscible in micelle accompanying a negative deviation from ideal mixing.

Taking into account the above bulk behaviour of mixtures of fluorocarbon and hydrocarbon surfactants, it is quite interesting to compare their three-dimensional bulk properties with the two dimensional surface properties. In addition, the mixed monolayers of perfluorocarbon and hydrocarbon fatty acids have not been reported yet other than the previous paper. In the present paper then, the surface pressure ( $\pi$ ) and the surface potential ( $\Delta V$ )-area (A) isotherms were obtained for mixed monolayers of different perfluorocarboxylic acids (FCs) with a hydrocarbon fatty acid, tetradecanoic acid (HC14) on substrate solution of pH 1.0 as a function of compositions in the mixture by employing the Langmuir method and the ionizing electrode method. The data for the mixed monolayers were analyzed in terms of the additivity rule. Judging from Matuo's classification of two dimensional phase diagrams, our phase diagrams might be classified into three types. *The first* is a positive azeotrope type; the combinations of tetradecanoic acid (HC14) with perfluorodecanoic acid (FC10) and with perfluorododecanoic acid (FC12) seem miscible with each other. *The second* is a completely immiscible type, the combination of perfluorotetradecanoic acid (FC14) and tetradecanoic acid. *The third* might be an eutectic type, to which the two combinations of HC14 with FC16 and with FC18 are assigned; they are miscible in the expanded state but immiscible in the condensed state. Furthermore, the data of the mean molecular area, the surface dipole moment, and the phase diagrams constructed enabled us to estimate the molecular orientation of the respective acids in the mixed monolayer state.

## 192.B3

COMPARISON OF ADSORPTION CHARACTERISTICS OF  
METHYL ORANGE AND  $\alpha$ -NAPHTHOL ORANGE MOLECULES  
ONTO THE DICATIONIC LANGMUIR-BLODGETT FILMS

Masashi Takahashi<sup>1</sup>, Koichi Kobayashi<sup>2</sup>, Kyo Takaoka<sup>2</sup> and Kazuo Tajima<sup>1</sup>

<sup>1</sup>Department of Chemistry, Kanagawa University, Yokohama 221, Japan

<sup>2</sup>Department of Chemistry, Musashi Institute of Technology, Setagaya, Tokyo 158, Japan

The adsorbability of dicationic LB films of N,N'- $\omega$ -*p*-xylylenebis(stearyl)dimethyl-ammonium chloride(XSAC) have been examined by using dye materials of methyl orange (MO) and  $\alpha$ -naphthol orange (NO) as adsorbates<sup>1,2</sup>. The structural characterizations of XSAC LB films with and without dye adsorption were also investigated by means of the spectroscopic methods and the X-ray diffraction analysis. In this study, we discussed the influence of ionic properties of dye molecules on adsorption characteristics of XSAC LB films, especially the difference between MO and NO adsorption.

It was found that XSAC LB films have fairly high adsorbability for negatively charged dye ions of MO and NO due to ionic interaction. X-ray diffraction measurements showed that the hydrocarbon chains in XSAC LB films took an interdigitated structure and that the bilayer thickness in the LB film was considerably enlarged by dye adsorption. Also, dye molecules penetrated in the XSAC LB film exhibited the remarkable difference in adsorbing state, i.e., MO molecules were arranged at the base of hydrocarbon chains with an edge-on orientation, while NO molecules existed around the polar head moieties of XSAC

layer with a lie-flat structure. Molecular ratios of XSAC to MO and NO in the dye-adsorbed XSAC LB film were 1.0:2.1 ~ 2.5 and 1.0 : 0.7 ~ 1.1, respectively, indicating that the adsorptions of MO and NO molecules occurred almost stoichiometrically in the LB films. Furthermore, these adsorption characteristics were compared with those of dye-complexed XSAC LB films which were fabricated with the monolayers spread on the aqueous dye solution. The molecular arrangements of XSAC and dye as well as the molecular ratio of XSAC to dye were confirmed to be almost the same in the different type of LB film.

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### 193.B3 PHASE TRANSITION AND MISCIBILITY IN MIXED ADSORBED FILM OF ALKANOL AND FLUOROALKANOL AT THE HEXANE/WATER INTERFACE

Takanori Takiue, Takehiko Matsuo, Norihiro Ikeda, Kinsi Motomura and Makoto Aratono  
*Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan*

It is generally known that the interaction between fluorocarbon and hydrocarbon chains is weak and therefore the fluorocarbon and hydrocarbon surfactants mix nonideally in the adsorbed film and micelle. The purpose of this study is to investigate the phase transition and miscibility of alkanol and fluoroalkanol mixture in the adsorbed film at the hexane/water interface from thermodynamic point of view.

We employed the 1-icosanol ( $\text{CH}_3(\text{CH}_2)_{19}\text{OH}$ ;  $\text{C}_{20}\text{OH}$ ) and 1,1,2,2-tetrahydroheptadecafluorodecanol ( $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{OH}$ ;  $\text{FC}_{10}\text{OH}$ ) mixture, because the phase transition takes place from the expanded to the condensed state in both adsorbed films of  $\text{C}_{20}\text{OH}$  and  $\text{FC}_{10}\text{OH}$ . The interfacial tension  $\gamma$  of the hexane solution of the mixture against water was measured as a function of the total molality ( $m$ ) and the composition of  $\text{FC}_{10}\text{OH}$  ( $X_2$ ) at 298.15 K under atmospheric pressure by the pendant drop method.

All the  $\gamma$  vs  $m$  curves have a break point (first break) which corresponds to the phase transition from the expanded to the condensed state. Furthermore, it was found that the curves at  $X_2=0.275$  and 0.280 show another break (second break) at high concentration. By calculating the interfacial densities ( $\Gamma^H$ ) and then drawing the interfacial pressure ( $\pi$ ) vs area per adsorbed molecule ( $A$ ) curves, it was suggested that the phase transition takes place from the expanded film to the condensed film of  $\text{C}_{20}\text{OH}$  in  $X_2 < 0.250$  and to that of  $\text{FC}_{10}\text{OH}$  in  $X_2 > 0.300$  at the first break point. Judging from the  $\pi$  vs  $A$  curves at  $X_2=0.275$  and 0.280, we concluded that the second break points correspond to the phase transition from the condensed film of  $\text{FC}_{10}\text{OH}$  to that of  $\text{C}_{20}\text{OH}$ .

To make the miscibility of alkanol and fluoroalkanol molecules in the mixed adsorbed film clearer, we evaluated the composition of the adsorbed film ( $X_2^H$ ) and drew the phase diagram of adsorption. It was found that the diagrams change their shapes from a positive azeotrope in the expanded state to a heteroazeotrope in the condensed state as the interfacial tension decreases. So it is concluded that  $\text{C}_{20}\text{OH}$  and  $\text{FC}_{10}\text{OH}$  molecules are practically immiscible in the condensed film because of the weak mutual interaction between them, while miscible with each other in the expanded film.

### 194.B3 PRESSURE EFFECT ON THE ADSORPTION OF FLUOROALKANOL AT THE HEXANE/WATER INTERFACE

Takanori Takiue, Shinji Ono, Atsuro Yanata, Norihiro Ikeda, Kinsi Motomura and Makoto Aratono  
*Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan*

It is known that fluorocarbon and hydrocarbon compounds are mutually soluble only at a limited composition range in their liquid and micellar states because of the weak interaction between the hydrophobic chains. The object of this study is to characterize the state of the adsorbed film of fluoroalkanols at the hydrocarbon oil/water interface and then to obtain the information on the interaction between hydrocarbon and fluorocarbon chains at the interface.

So we employed partially fluorinated alcohols,  $\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_2\text{OH}$ , ( $n=5$ ;  $\text{FC}_8\text{OH}$ ,  $n=7$ ;  $\text{FC}_{10}\text{OH}$ ,  $n=9$ ;  $\text{FC}_{12}\text{OH}$ ) and measured the interfacial tension ( $\gamma$ ) of the hexane solution of alcohols against water as a function of pressure ( $p$ ) and molality ( $m_l$ ) at 298.15 K by the pendant drop method. The  $\gamma$  value increases slightly in a low concentration and low pressure region and decreases greatly in a high concentration region with increasing pressure. The important point is that the two kinds of break points were observed on the  $\gamma$  vs  $p$  and  $m_l$  curves of the  $\text{FC}_8\text{OH}$  and  $\text{FC}_{10}\text{OH}$  systems and, on the other hand, only one on those of the  $\text{FC}_{12}\text{OH}$  system. The above results were analyzed by using the thermodynamics of interfaces.

The value of interfacial density ( $\Gamma_1^H$ ) of fluoroalkanols increases with increasing molality and changes discontinuously at concentrations corresponding to the breakpoints on the  $\gamma$  vs  $m_l$  curves. By drawing the interfacial pressure ( $\pi$ ) vs area per adsorbed molecule ( $A$ ) curves, it was confirmed that the two types of phase transitions take place from the gaseous to the expanded state and from the expanded to the condensed one in the adsorbed films of  $\text{FC}_8\text{OH}$  and  $\text{FC}_{10}\text{OH}$ . On the other hand, in the adsorbed film of  $\text{FC}_{12}\text{OH}$ , it is found that the phase transition takes place only from the gaseous to the condensed state.

To make clear the influence of the fluorocarbon chain on the volumetric behaviour of fluoroalkanol at the hexane/water interface, we evaluated the volume change associated with adsorption  $\Delta v$ . It was found that the value of  $\Delta v$  decreases from positive to negative with increasing adsorption. Furthermore, by estimating the partial molar volume change of adsorption of the alcohol, it was suggested that the increase in the partial molar volume of alcohol with increasing fluorocarbon chain length is larger in the solution than in the interface because of the weak mutual interaction between fluoroalkanol and hexane molecules.

### 195.B3 METHOD OF PURIFICATION AFFECTS SOME INTERFACIAL PROPERTIES OF PULMONARY SURFACTANT PROTEINS B AND C, AND THEIR MIXTURES WITH DPPC

S. Taneva, J. Stewart, L. Taylor, K. M. W. Keough

*Departments of Biochemistry and Pediatrics, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X9 Canada*

Two methods of preparation of lipid extract surfactant were employed for isolation of surfactant proteins SP-B and SP-C from porcine lung surfactant. Spread monolayers at the air-water interface of SP-B or SP-C isolated from butanol lipid extracts showed larger molecular areas than those determined in films of SP-B or SP-C isolated from chloroform-methanol surfactant extracts. Aqueous dispersions of dipalmitoylphosphatidylcholine (DPPC) supplemented with 2.5 wt% and 5.0 wt% of SP-B or SP-C obtained from butanol extracts adsorbed faster to the air-water interface than their counterparts reconstituted with proteins isolated from chloroform-methanol extracts. Surface pressure-area characteristics of spread monolayers of DPPC plus SP-B or SP-C seemed not to depend on the method of isolation of the proteins. The diagrams of the mean molecular areas versus composition for the monolayers of DPPC plus SP-B or SP-C showed positive deviations from the additivity rule independently of the procedure used for preparation of lipid extract surfactant. Matrix assisted laser desorption/ionization spectrometry (MALDI) of the proteins was consistent with some changes in the chemical compositions of the proteins. Butylation or methylation of the proteins during extraction of surfactant pellet with butanol or methanol may account for the observed differences in the molecular masses of the proteins. The study suggests a role of the method of isolation of the hydrophobic pulmonary surfactant proteins in their property to enhance the adsorption rates of DPPC/protein mixtures which may have a relevance to the utilization of protein-supplemented lipid formula during exogenous treatment of pulmonary surfactant insufficiency in vivo (Supported by Medical Research Council of Canada).

## 196.B3 ALLOWING FOR ORIENTATION STATES OF ADSORBED MOLECULES IN ADSORPTION THEORY ON HETEROGENEOUS SURFACES

Yu.K. Tovbin

*Karpov Institute of Physical Chemistry, Moscow, Russia*

The theoretical description of adsorption systems is complicated if there can be various orientation states of adsorbed molecules. Most molecules are nonsymmetric, therefore, in various orientations there should be disposed on different numbers of adsorption centers. Such problem to describe adsorption of the molecules disposing more than one adsorption center is one of the hard to the moment. Earlier it was considered mainly for flat homogeneous interfaces [1-3].

With use of the cluster method [4,5] we suggest a general way to construct the closed systems of equations that enables us to describe adsorption processes with allowing for different orientation states of large molecules on heterogeneous surfaces. To the present time the cluster approach is the only way to take into account influence of the various types of microheterogeneities on the surfaces differing by structure and chemical compositions of substrates. (Today, only pairwise and chaotic heterogeneous surfaces are taken into account even for one-center molecules.) The equations are given which describe equilibrium distribution of adsorbed molecules with simultaneous allowing for both surface microheterogeneity of solids and lateral interactions between molecules.

At low surface coverages these equations extend the earlier obtained in ref. [1] to heterogeneous surfaces. It is shown that even in this case the multidimensional distribution functions that characterize the pairs and clusters of adsorption centers over both energy and space have to be used. For the two dimensional lattice the lateral interactions are included through the quasichemical or mean-field approximations.

The extension of the theory on a case of multilayer adsorption has been performed.

Applications of the developed theory to flat homogeneous and heterogeneous nonporous systems as well as porous systems are discussed. Effects of orientation states and surface microheterogeneity of solids on local distribution of adsorbed molecules, isotherms and adsorption heat are considered. The comparison of the contributions from different orientations in the benzene/graphite system made for both molecular dynamics [6] and lattice model gives a good agreement. It has been shown that a confine space in pores and a heterogeneity of their wall affects the conditions of capillary condensation in slit-like pores. Effects of a pore width on orientation states of benzene molecules in narrow pores as well as applicability of the Dubinin- Radushkevich equation for the volume filling of micropores in wide range of pressure in gas phase, for which the benzene molecules usual serve as reference system, are investigated. Area of its reasonable use is determined.

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## 197.B3 THEORETICAL INVESTIGATION OF WATER SORPTION IN PERFLUORINATED SULFOCATIONIC MEMBRANES

Yu. K. Tovbin, N. F. Vasyutkin

*Karpov Institute of Physical Chemistry, Moscow, Russia*

A water sorption process in the perfluorinated sulfocationic membranes (PSM) is of interest from the point of view of study of formation of monolayer and multilayer filling in strongly nonuniform environments and influence of a character of the filling on the diffusion characteristics of a membrane permeability. In the practice tasks the interest to the PSM for the experimental and theoretical investigation is due to unique properties (high chemical and thermal firmness, high permissible current density) [1].



At this work the macroscopic characteristics of the water diffusion in the pores of PSM on the theoretical methods are investigated. The pore presents a split structure formed by closely packed polymers with side chains including  $\text{SO}_3$  groups and directed other to other [2]. The interparticle potentials created on the quantum-chemical MNDO calculations are used in the PSM-cation-water system's potential energy calculation [3]. This potentials take into account the redistribution of electronic density on the particles and the changing of the geometry of sulfogroup when cation displaced. By the minimizing of the potential energy of the system the localization of water molecules in hydrate shell of cation Li in the pore at the different water contents  $n \text{ SO}_3/\text{H}_2\text{O}$ , (from 0 to 10) was studied.

Influence of the water content of a membrane on character of distribution of molecules of a water is investigated. At small quantity of a water clusters are at first formed around of the cations. As far as they are crossing water layer connecting water molecules of opposite chains or between chains from each side of the pore space is formed. And at last, multilayer filling of the pore space of a membrane occurs further. In particular, nearest to the cation three molecules of a water will form a rigid structure - a hydrate environment, the properties of which essentially differ from properties of the other molecules of a water. These molecules migrate with the cation as a unit. For cation migration availability of sufficient number of molecules of a water, ensuring by continuous translation movement on a pore is necessary.

On the calculated water distributions a lattice of hydrogen bonds was created. With lattice model [4] a macroscopic characteristics such as the constant of Henry, isotherm of sorption, diffusion of water molecules, spectroscopic characteristics are calculated. The temperature and concentration dependencies of calculated values are investigated. The results are comparing with experimental data and the results of the simulations methods.

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## 198.B3 EXPERIMENTAL EVIDENCE AND THEORY FOR PHASE TRANSITION IN ADSORPTION LAYERS AT THE AIR-WATER INTERFACE: BRIDGING TO LANGMUIR MONOLAYERS

D. Vollhardt, V. Melzer, V. Fainerman

*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Berlin, Germany*

This work provides the first conclusive evidence that a first order phase transition can occur in adsorption layers. For studying the general conditions for the formation of a two-phase coexistence in adsorption layers a special tailored amphiphile N-dodecyl- $\gamma$ -hydroxy-butyric acid amide (DHBAA) which can also be spread as a Langmuir monolayer has turned out to be optimal.

Adsorption layers of aqueous solutions of the amphiphile DHBAA are investigated using surface pressure ( $\pi$ ) measurements, Brewster angle microscopy (BAM) and Synchrotron X-ray diffraction at grazing incidence (GID).

During the adsorption kinetics, the phase transition is indicated thermodynamically by an inflection point in the continuous course of the  $\pi(t)$  transients. Appearance and location of the phase transition point depends largely on the concentration of the amphiphile in the aqueous solution and on the temperature. If a phase transition occurs in an adsorption layer the formation of condensed phase patterns surrounded by the homogeneous fluid-like phase are visualized by BAM. According to the measurements of the integral reflectivity signal, there is an induction time between the thermodynamic phase transition and the growth of condensed phase patterns on the microscopic scale. During the induction time, the size of the condensed phase nuclei newly formed is not large enough to be visualised microscopically by BAM.

Different types of morphological textures of the condensed phase can be formed depending on the temperature such as two types in DHBAA monolayers above and below  $10^\circ\text{C}$ . Detailed information on the orientational order of the domain textures are obtained by rotating the analyser in the reflected laser beam. The main growth directions of the condensed phase textures are correlated to the lattice structure obtained by GID. The tilt direction of the alkyl chains is parallel to the two main growth directions.

The experimental bridging to the Langmuir monolayers supports the conclusions of a first order main transition drawn from the adsorption kinetics studies. The phase transition points in the  $\pi(t)$  transients correspond to the main transition points of the  $\pi$  - A isotherm. In the same temperature region, the textures formed in the two-phase region of the  $\pi(t)$  transients and the plateau region of the  $\pi$  - A isotherms agree completely in the main morphological properties.

A theoretical model has been derived which describes the adsorption kinetics of the two-dimensional first-order phase transition in an adsorption layer. The theory includes a kinetic model of the phase transition in Langmuir and Gibbs monolayers, the adsorption from the bulk solution and the dissociation kinetics of the bulk micelles.

The analysis of the dynamic surface pressure ( $\pi$ )- area (A) experiments involves a description of the main phase transition between the gas-like phase and the condensed phase and is based on a new equation of state derived by us. This equation considers the formation of two-dimensional aggregates and describes the non-horizontal plateau region of the  $\pi$  - A isotherm for the two-phase coexistence.

### 199.B3 PLASMA SPRAYING TECHNOLOGY AND ITS APPLICATION

**Zhang Wenhua, Zao Shangquan, Hu Zhengqian**

*Wuhan University of Technology, Wuhan, P. R. China*

Surface coating technology which was one of ten key technologies in the world in 1980's is now an important part of surface engineering. Regarded as high-technology, thermal spraying technology has been developed with emphasis in China. Among them plasma spraying is a mature and economic technology to coat the surface of materials. It can coat any materials which can be melted and softened on any substrates. Since 1980's it has been becoming a hot point of research on surface coating technology. In this paper the development of plasma spraying technology since the ITSC'95 conference is briefly summarized. Emphasis was placed on the new achievements of plasma spraying materials, processing, coating properties, facilities and application. The state of the plasma spraying technology in China is also introduced in the paper.

### 200.B3 INVESTIGATION OF MEASUREMENT OF INTERNAL STRESSES OF METAL MULTILAYER COMPOSITE COATINGS

**Gu Zhuoming**

*Merchant Ship Institute of Shanghai Maritime University, Shanghai, 200135, China*

The principle, formula and determination of internal stresses of metal multilayer composite coatings by means of the bending strip method were studied. Using this method, internal stresses of ion-plated metal multilayer composite coatings and thick monolayer coating of aluminium bronze, stainless steel and nickel-iron alloy were determined. The reason of decreasing of internal stresses of multilayer composite coatings was discussed.

### 201.B4 EVALUATION OF ACID-BASE SURFACE PROPERTIES OF STYRENE-ACRYLONITRILE RANDOM COPOLYMERS FROM CONTACT ANGLE MEASUREMENTS

**Marina Helena C.V. Adão, Benilde J.V. Saramago and Anabela C. Fernandes**

*Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa Codex, Portugal*

The solid surface tension,  $\gamma_s$ , is a fundamental property of materials and determines their surface and interfacial behaviour in processes like adsorption, wetting and adhesion. However, this surface tension is not a directly measurable quantity. One of the most used methods to estimate  $\gamma_s$  is based on contact angle

measurements. The aim of this study is to evaluate the solid surface tension of a series of styrene-acrylonitrile random copolymers with variable composition and to determine the Lifshitz-van der Waals,  $\gamma^{LW}$ , and acid-base,  $\gamma^+$  and  $\gamma^-$ , components using the approach developed by Van Oss et al (1,2). The determination of the dispersive,  $\gamma^d$ , and polar,  $\gamma^p$ , components of the solid surface tension for this series of copolymers and the comparison with the  $\gamma^{LW}$ ,  $\gamma^+$  and  $\gamma^-$  components using the Van Oss' approach and water, glycerol and diiodomethane as the test liquids was the objective of a previous study (3). However, this comparison was only possible for polystyrene and for the copolymer containing 2% by weight in acrylonitrile. For higher acrylonitrile concentrations the diiodomethane is not adequate because a reaction occurs between the substrate and the liquid. In the present study the contact angles of water, glycerol and thiodiglycol, together with their  $\gamma^{LW}$ ,  $\gamma^+$  and  $\gamma^-$  components were used in a modified Young-Good-Girifalco-Fowkes equation (1,2) to calculate the solid surface tension components of the copolymers having an higher content in acrylonitrile. The liquid surface tension components,  $\gamma^{LW}$ ,  $\gamma^+$ , and  $\gamma^-$  for thiodiglycol, which are not reported in the literature, were determined from contact angle measurements on three polymeric substrates: polystyrene, styrene-acrylonitrile copolymer with 2% by weight in acrylonitrile and polymethylmethacrylate. The acid-base character of the copolymers surface was evaluated as a function of the bulk chemical composition of the substrates.

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## 202.B4 MEASUREMENT OF THE ADHESION ENERGY OF SURFACES COVERED WITH A THIN LAYER OF ADSORBED LIQUID

E. Barthel<sup>1</sup>, J.L. Loubet<sup>2</sup>

<sup>1</sup>Laboratoire CNRS/Saint-Gobain "Surface du Verre et Interfaces", 39, quai Lucien Lefranc, BP 135, F-93303 Aubervilliers Cedex, France

<sup>2</sup>Laboratoire de Technologie des Surfaces, URA CNRS 855, Ecole Centrale de Lyon, 36, avenue Guy de Collongue, BP 163, 69131, Ecully Cedex, France

The adhesion energy of surfaces covered with a thin layer of adsorbed liquid is a problem of substantial technological impact, mainly in the field of ceramics and oxide processing. Measuring adhesion energies with the surface forces apparatus (SFA) typically requires the measurement of some pull-out force<sup>1</sup>. Generally, the adhesion energy is deduced from the pull-out force using the theory due to Derjaguin, Muller and Toporov (DMT)<sup>2</sup>. In this paper, we show that in the case of small menisci (i.e. thin films), this approach is no longer valid.

We have measured the force vs. penetration curves for silica surfaces in dry atmosphere, using a rigid SFA<sup>3</sup>. A thin layer of anomalous water was found to be adsorbed on the surfaces. We have determined both the pull-out force and the steep attractive interaction due to the meniscus after contact break-up.

The attractive interaction allows one to determine the surface energy of the liquid and its contact angle with the solid.

In addition, knowing the long-range interaction profile, we can accurately model the contact, using a self-consistent approach<sup>4</sup>. We find that in our case: 1) the data can not be described by a DMT model, nor a Johnson, Kendall and Roberts model<sup>5</sup>, but by an intermediate case 2) we can measure an small "additional" adhesion, which is not due to the long-range interaction, and characterizes the very short range contribution to the adhesion. This very short range attraction cannot be measured directly.

Conclusion: in the case where liquid films are adsorbed, accurate description of the point contact between surfaces may require the use of a more sophisticated model than DMT. Using a rigid SFA, one can measure the steep long range interaction and compute its contribution to the adhesion. One can therefore deduce an "additional" contribution due to the very short range attractive interactions. This approach can be generalized to any type of interaction.

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## 203.B4

### DEWETTING ON ELASTOMERIC SOLIDS OF DIFFERENT CROSSLINKING DENSITY

Alain Carré<sup>1</sup>, Martin E.R. Shanahan<sup>2</sup>

<sup>1</sup>*Corning Europe Inc., 7 bis, Avenue de Valvins, 77210 Avon, France.*

<sup>2</sup>*Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris,  
Centre des Matériaux P.M. Fourt, BP 87, 91003 Evry Cédex, France.*

The kinetics of spreading of a liquid drop on a rigid solid substrate is usually controlled by conversion of capillary energy into viscous dissipation within the liquid. However, if the substrate is a soft rubber, a "wetting ridge" forms at the solid/liquid/vapor triple line and motion of this ridge leads also to viscoelastic dissipation which reduces considerably the liquid spreading speed. Similar arguments apply for dewetting of an unstable thin liquid film in which dry holes grow at a rate depending mainly on the damping properties of the substrate when this latter is an elastomer. Existence of the wetting ridge in wetting and dewetting on a rubber has been confirmed using Scanning Interferometric Microscopy. Its height is of the order of  $\gamma \sin \theta_0 / G$ , where  $\gamma$  is the liquid surface tension,  $\theta_0$ , the Young contact angle and  $G$  the shear modulus of the elastomeric substrate. Considering that  $G \sim M_c^{-1}$ ,  $M_c$  being the average intercrosslink molecular weight of the rubber, the local deformation and the dissipative properties of the substrate ( $\tan \delta$ ) can be modified by changing its degree of crosslinking ( $M_c$ ). This possibility is illustrated with a series of silicone rubbers of different crosslinking density on which a nonviscous liquid dewets at different rates,  $U$ . Therefore a simple law between  $U$  and  $M_c$  is proposed and verified.

## 204.B4

### POLYMER ADHESION ON ANODIZED ALUMINIUM: PENETRATION AND ADSORPTION OF POLYMERS IN NANOSIZE CAPILLARIES

S.G.O. de Haas<sup>1</sup> and G. Frens<sup>2</sup>

<sup>1</sup>*Adhesion Institute, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands*

<sup>2</sup>*Laboratory of Physical Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft,  
The Netherlands*

A method has been developed for measuring the penetration depth and adsorption of fluid polymers in nanosize capillaries. After pressurization moulding a polymer melt against anodized aluminium, the aluminium and aluminium oxide are dissolved in a sodium hydroxide solution and a nitric acid solution. Contact angle measurements on the thus obtained polymer plate provide information on surface energy and polymer adsorption. The penetration depth can be measured by fractography on SEM after fracturing the polymer plate in liquid nitrogen.

This method has been used for the investigation of polymer adhesion on aluminium. In order to obtain a good adhesion, the aluminium has to be pretreated. This can be done by successive degreasing, pickling and anodizing of the aluminium. The result is a porous oxide layer with pore diameters of about 40 nm. Exposure of anodized aluminium before applying an organic coating reduces the polymer-metal adhesion quality. Decrease of the polar component of the aluminium surface energy immediately following pretreatment will result in less adsorption and pore penetration of the polymer in contact with this substrate. This is indeed what is found experimentally.

## 206.B4 IMPROVED GLASS-LATEX FILM ADHESION UNDER WET ENVIRONMENTS, BY USING AN ALUMINUM POLYPHOSPHATE FILLER

Elizabeth F. de Souza and Fernando Galembeck

*Universidade Estadual de Campinas, PO Box 6154, 13083-970 Campinas SP, Brazil*

A major problem in the use of adhesives is joint failure, under high humidity conditions. In the case of polymer adhesion, oxidation is often used as a substrate surface preparation step; the oxidation products formed are polar, for which reason the interfaces undergo swelling to a higher extent than other parts of the joint. This leads to local pressure and tension gradients, which finally contribute to failure. The problem may still be increased by the hydrolysis of covalent bonds (e.g., ester or amide bonds) formed by reactive groups, or preexisting in the oxidized surface and in the adhesive.

A class of chemical bonds which is extremely water-resistant but which has been seldom used in the making of strong adhesive joints are ionic bonds between multi-charged ions. This is largely due to the difficulty of obtaining organic cations or anions with multiple charges. For this reason, ionic bonding is never considered to be as important in the making of strong joints as, for instance, acid-base interactions.

We have approached this problem by using a new inorganic filler for water-based adhesives, amorphous aluminum polyphosphate (PFAI). Our interest in this compound was initially derived from its self-opacifying properties, in water-based latex paints. This led to an extensive series of experiments, during which we noticed that adhesive properties of poly(vinylacetate) latex (PVAc) films are greatly improved, when the films were cast from the PFAI-latex dispersions are used.

In this work, we report on the improvement of latex film-to-glass surface adhesion, using amorphous aluminum polyphosphate as a latex filler (50% on a volume basis), as compared to unfilled latex, and to  $\text{TiO}_2$ -filled latex.

PFAI-PVAc dispersions were prepared, cast according to ASTM-D 823-87 (method E) on glass panels and slides, and dried under air. Incisions were made in the dry film surfaces, following ASTM-D 3359-87 standard. In the case of  $\text{TiO}_2$ -filled PVAc, grid incision by itself was already sufficient to strip almost all of the coating, from the glass surface. This was not observed in the unfilled and in the PFAI-filled films.

The unfilled film underwent considerable swelling under 24 h immersion in water and peeled off spontaneously, both in the incised area and beyond. The PFAI-PVAc film adhesion to glass was unaltered by immersion in water and dimensional changes associated to swelling were less than 1%.

A detailed examination on the PFAI-PVAc composite film was made by electron microscopy, X-ray microprobe analysis and by spatially-resolved Raman microspectroscopy. This reveals that the PFAI and the PVAc domains both percolate throughout the solid film, which can then be described as a bicontinuous network. This observation reveals that the organic and inorganic phases are highly compatible, which is assigned to the formation of aluminum ion bridges, connecting the negative ionic groups from both the latex and the polyphosphate domain surfaces.

The strong composite film adhesion to glass is also interpreted as the result of aluminum ions bridging the film and the glass negative surfaces. These results show a new, successful approach for making water-resistant adhesive joints.

## 207.B4 DYNAMICS OF SPONTANEOUS SPREADING WITH EVAPORATION ON A DEEP FLUID LAYER

Anne D. Dussaud and Sandra S. Troian

*Princeton University, Dept. of Chemical Engineering, Princeton, NJ 08544, USA*

The spontaneous spreading of thin volatile films along the surface of a deep fluid layer is an important transport mechanism in many technological applications. This spreading process is used, for example, as a carrier mechanism in the casting of biological and organic Langmuir-Blodgett films. We have investigated the dynamics of spontaneously spreading volatile films of different vapor pressures and spreading coefficients advancing over the surface of a thick water support. Laser shadowgraphy was used to

visualize the entire surface of the film from the droplet source to the leading edge. Previous studies of the dynamics in non-volatile, immiscible thin films spreading on a thick liquid support have shown that the leading edge advances in time as a power law with an exponent  $3/4$ , as predicted by laminar boundary theory. We have found that the leading edge of volatile and relatively immiscible spreading films also advances as a power law but with an exponent  $1/2$ . Differences in the liquid vapor pressure or the spreading coefficient seem only to affect the speed of advance but not the value of the spreading exponent. Side view laser shadowgraphs depicting the subsurface motion in the water reveal the presence of a single elliptically shaped circulation pattern beneath the leading edge of the spreading film. This flow is likely caused by evaporation and surface cooling accompanying the rapid spreading and may be related to a propagating Benard-like convective roll. Such circulation pattern may provide the additional dissipative mechanism responsible for the decrease in the spreading exponent from  $3/4$  to  $1/2$ .

## 208.B4

### CONTACT ANGLE HYSTERESIS ON POLYMER SURFACES

C.W. Extrand

*Fluoroware, Chaska, MN, USA*

Contact angle hysteresis, or the difference between advancing and receding contact angles, is usually attributed to roughness, surface heterogeneity, or overturning of molecular segments at the surface (1). Although contact angle hysteresis has been widely studied, the fundamental underlying causes still are not completely understood.

In earlier work (2), preliminary evidence was found that contact angle hysteresis may not be an extensive property. In this study, advancing and receding contact angles of four organic liquids and water were measured on a variety of polymer surfaces and silicon wafers using an inclinable plane. Contact angles varied widely from liquid to liquid and from surface to surface. Surface roughness was found to be relatively unimportant, rather the contact angles seemed to be more closely tied to the chemical nature of the surfaces.

Thermodynamic expressions for the free energy of contact angle hysteresis were derived and experimental data were used to calculate free energies. For each surface, a variety of organic liquids and water gave a single value of free energy. Non-polar polymer surfaces had roughly the same value of free energy, corresponding to van der Waals interactions or bonding. These findings suggest that it might be possible to explain hysteresis simply in terms of molecular interaction without having to invoke surface non-idealities such as heterogeneities, roughness, swelling, deformation, etc.

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## 209.B4 LIQUID BINARY MIXTURES: SPREADING INDUCED BY EVAPORATION

Xavier Fanton, Anne-Marie Cazabat

*Physique de la Matière Condensée, Collège de France, 11, place Marcelin Berthelot,  
75231 Paris Cedex 05 France*

Binary mixtures of liquids of different volatility and different surface tension can spontaneously exhibit strong convective effects. When the more volatile component has a lower surface tension, a concentration gradient built up by evaporation induces a surface tension gradient which drives the liquid up on a tilted wall (Marangoni effect) [1-3].

The spreading process was systematically studied for three alkane mixtures: hexane/dodecane, heptane/dodecane and octane/dodecane. The length of the climbing film was found to follow a diffusive-like law, and a characteristic Rayleigh-like instability was observed at the meniscus between the reservoir and the climbing film. We developed a model to describe the influence of the volatility and the concentration on the spreading, which satisfactorily accounted for the behavior of the (ideal) alkane mixtures. Moreover, the

same model explained successfully the very specific behavior previously observed [1] for the non-ideal ethanol/water mixture.

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## 210.B4

### SURFACTANT ENHANCED SPREADING

R.M. Hill<sup>1</sup>, T. Stoebe<sup>2</sup>, M.D. Ward<sup>2</sup> and H.T. Davis<sup>2</sup>

<sup>1</sup>*Dow Corning Corporation, Midland, MI 48686, USA*

<sup>2</sup>*CEMS, University of Minnesota, Minneapolis, MN 55455, USA*

Recent studies of the unusual rapid spreading behavior of aqueous dispersions of the trisiloxane polyoxyethylene surfactant M(D'E8)M have shown that there is a maximum in spreading rate as a function of surfactant concentration and substrate surface energy. We have now extended this work to ionic and nonionic organic surfactants and have found examples of nonionic and ionic organic surfactants which also exhibit rapid spreading of aqueous films over relatively hydrophobic surfaces. In all cases, the spreading rates depend strongly on surfactant concentration, substrate surface energy, roughness, and, in some cases, relative humidity. The generality demonstrated by the variety of surfactants exhibiting this behavior provides insight into the spreading mechanism. The results demonstrate that spreading is driven by Marangoni flow. A correlation has been found between solubility or turbidity and spreading - those materials which form turbid dispersions seem to provide the most rapid spreading. In this case turbidity is due to the presence of a dispersion of bilayer vesicles. The presence of vesicles contributes to the low dynamic surface and interfacial tensions at short time scales, leading to the ability to spread more rapidly.

## 211.B4

### THE EFFECT OF THERMAL TREATMENT OF SILICA ON ITS SURFACE FREE ENERGY COMPONENTS

Lucyna Holysz and Emil Chibowski

*Department of Physical Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University,  
20031 Lublin, Poland*

The stock sample of silica gel 100 (Merck), for column chromatography (particle size 0.063-0.2mm), was heated at 200°C for 2 h, and then parts of this sample used were heated at 400, 600, 800 and 1000°C also for 2 h. The surface free energy components of such treated the samples were determined by wicking method, i.e. from the rate of penetration of apolar (n-octane, n-nonane, n-decane and diiodomethane) and polar (water and formamide) liquids into the powder columns packed in glass capillaries of 10 cm long and 2 mm of the inner diameter. The values of Lifshitz van der Waals,  $\gamma_s^{LW}$ , as well as acid-base; electron donor,  $\gamma_s^-$ , and electron-acceptor,  $\gamma_s^+$ , components of the silica surface free energy were determined from a modified Washburn's equation [1-3]. A slight increase in  $\gamma_s^{LW}$ , from 42.0 to 47.7 mJ/m<sup>2</sup>, was observed for the samples treated at 200 and 400°, respectively. However, this component decreased to 45.0 mJ/m<sup>2</sup>, for the samples treated at higher temperatures. Elimination of the surface silanol groups (i.e. principal adsorption sites responsible for the adsorption caused by hydrogen bonding) resulted in changes of acid-base components. From the determined values of  $\gamma_s^-$  and  $\gamma_s^+$  for the particular samples, the prevalence of the electron-donor (Lewis base) properties of silica surface clearly results. The interactions had weakened upon the increasing temperature of the sample pretreatment. The  $\gamma_s^-$  decreased from 58.4 to 23.8 mJ/m<sup>2</sup>, and it was accompanied by an increase in electron acceptor component, from 0.2 to 3.1 mJ/m<sup>2</sup>, for 200 and 800°C, respectively. It should be stressed that treatment of the sample at 1000°C caused not only dehydroxylation of the surface but also some structural changes appearing in a decreased the specific surface. Because the studied sample of the silica gel had acidic properties, the observed changes in the acid-base interactions may be interpreted in terms of the adsorption of water molecules, which form the hydrogen

bonds with the oxygen atoms of the surface silanols. The samples after heating them to particular temperatures had a contact with water vapor present in the atmosphere during the wicking experiments. Such the model of water molecules adsorption is in agreement with the literature[4]. It is interesting that the decrease in the  $\gamma$  component is practically linear with the decrease in the number of -OH groups/nm<sup>2</sup>, which changes from 4.6 (200°C treated sample) to 0.7 (800°C treated sample) [4]. Taking the minimum literature value of the hydrogen bonding energy (10kJ/mol) and the determined acid-base components for the tested samples, the numbers of the surface electron donor and electron acceptor silanols were calculated. A good agreement with the literature data given above has been found.

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## 212.B4

### CONVECTIVE-DIFFUSIVE MEAN-FIELD MODELS OF WETTING DYNAMICS

Adil A. Khan<sup>1</sup>, Terence D. Blake<sup>2</sup> and Yitzhak Shnidman<sup>3</sup>

<sup>1</sup>*University of Rochester, Rochester, New York 14627, USA*

<sup>2</sup>*Kodak Limited, Harrow, Middlesex HA1 4TY, England*

<sup>3</sup>*Eastman Kodak Company, Rochester, New York 14650, USA*

We have recently developed novel convective-diffusive lattice-gas models to study the time evolution of interfaces in two-phase systems wetting a solid substrate. Lattice-gas representations of microscopic interactions and kinetic energies are used as the starting point. As in lattice-Boltzmann methods, time evolution of local species and momentum densities consists of alternating convective and dissipative steps subject to local conservation laws. However, in contrast with the lattice-Boltzmann methods, where the dissipative step is implemented by lattice collision rules without explicit dependence on microscopic interactions, in our models the dissipation is of diffusive origin, with an explicit, strong dependence on microscopic interactions. At solid boundaries, no-slip boundary conditions are used during the convective step, thus causing momentum transfer at the walls. During the subsequent diffusive step, dissipative relaxation of interfaces towards equilibrium gives rise to velocity slip at an interfacial zone of finite width near the wall, as in the molecular-kinetic theory of dynamic wetting. Unlike the latter, however, our model incorporates convective flows and local momentum conservation, as in classical hydrodynamic models of dynamic wetting, though in our case the interfacial properties vary smoothly over a zone of finite width, rather than being discontinuous or singular at a sharp (infinitesimally thin) interface.

The first part of the talk will review the derivation of the isothermal version of the convective-diffusive evolution equations for one- and two-species fluid systems in a sheared microcapillary. Numerical applications of these equations for studying the time evolution and nonequilibrium steady-states of simple liquid-liquid and liquid-vapor systems will be discussed and tested against known behavior such as the Young-Laplace law, capillary wave dispersion relations, molecular dynamics simulations and experimental studies.

In the second part of the talk we will present results of systematic studies of the variation of the dynamic contact angle as a function of the ratio between fluid-fluid and solid-fluid interactions and of the contact line velocity relative to the substrate, for two situations: (a) spreading drops, and (b) steady-state drops in sheared microcapillaries.

We will conclude with a discussion of possible generalizations of this microscopic approach for application towards more complex fluids, and of its connections to mesoscopic convective diffusive equations of the time-dependent Landau-Ginzburg type, such as coupled Cahn-Hilliard and Navier-Stokes equations (also known as Model H in the literature).



## 213.B4

SLIPPAGE OF CTAB SOLUTIONS FLOWING THROUGH  
THIN QUARTZ CAPILLARIES

O.A. Kiseleva, V.D. Sobolev, N.V. Churaev

*Institute of Physical Chemistry RAS, Moscow, Russia*

The phenomenon of slippage takes place when a liquid flows in lyophobic capillaries. Such effects were observed for mercury in glass capillaries [1] and for water in methylated quartz capillaries [2]. The reason for slippage is a reduction of adhesion of liquids possessing of strong intermolecular bonds.

In this work the flow rates of cationic surfactant solution (CTAB) in thin quartz capillaries at pH 6.5, when capillary surface is negatively charged, were measured. Due to electrostatic adsorption of  $\text{CTA}^+$  ions the surface of quartz becomes hydrophobed. Maximum values of advancing contact angles are of about  $70^\circ$  in concentration range of CTAB solution  $10^{-5}$  -  $10^{-4}$  M, when isoelectric point of quartz surface was reached.

The flow rates  $V$  were measured observing using a microscope device the rate of motion of a meniscus under an applied pressure difference  $\Delta P$ . As earlier [3], the measurements were performed at practically constant length  $l \sim 7\text{--}8\text{ cm}$  of liquid in the capillary, when meniscus moves in both direction with in a small portion of the capillary (0.1-0.2 mm). In the experiments thin quartz capillaries with radii 0.71 and 0.89  $\mu\text{m}$  were used, on the same order of sizes as in the previous work [2].

In the course of subsequent flow measurements capillary surface becomes gradually hydrophobed and hysteresis of contact angles develops. However, the  $V(\Delta P)$  dependencies remain linear corresponding to some constant value of viscosity  $\eta$ . Comparing the slopes of the graphs with that of pure water, some deviation from bulk water viscosity  $\eta_0$  were observed when contact angle approaches to  $70^\circ$ . Calculated values of  $\eta$  in all the cases are lower than  $\eta_0$ . This gives the possibility to assess the value of the slip coefficient  $\gamma$  from the equation  $\eta_0/\eta = 1 + (4\eta_0\gamma/r)$ , where  $r$  is the capillary radius.

The preliminary results have shown, that the ratio  $\eta_0/\eta$  is higher than 1, and the values of  $\gamma$  are on the order of  $10^{-5} \text{ m}^3/\text{N}\cdot\text{s}$ , approaching at contact angle  $70^\circ$  the values of  $\gamma$  determined in the work [2]. Therefore, the effect of slippage exists not only in methylated quartz capillaries, but also in the presence of adsorbed layers of CTAB render the quartz surface hydrophobic.

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## 214.B4

ON SURFACE TENSION  
A COMMON CONCEPT, OFTEN EXPLAINED USING A FALSE MODEL

Vladimir León

*INTEVEP, S.A. Res. & Tech. Support Center of Petróleos de Venezuela, S.A. (PDVSA),  
P.O. Box 76343 Caracas 1070A Venezuela*

The concept of surface tension is many times introduced as a force per unit length originated from the "stress tensor" at the liquid surface (and vaguely extended to solids). This model, a paradigm for many workers in the field, is wrong. The inferences from the model, however, are correct in the more common uses, some contradictions may appear but not big enough to abandon such simple and intuitive concept. The origin of the surface tension, of a liquid or solid surface, is in the molecular interactions available when some other condensed phase is put in contact with such a surface. Recent developments using the surface tension components allow to predict interfacial surface tensions and to measure surface tension of solids. Although the power of this approach is evident, its use is only incipient because some results, particularly the presence of negative interfacial tensions, are difficult to interpret using the erroneous vision of surface

tension as a consequence of the stress tensor at the liquid (or solid) surface. We present here some properties of liquids useful to fundament the concept of surface tension and briefly refer to Laplace equation, Young equation and capillarity, trying to correct some misinterpretations.

## 215.B4 DETERMINATION OF THE SURFACE TENSION OF SOLIDS: I. THE PLATINUM CASE

Vladimir León, Alfonso Carolina Araujo

*INTEVEP, S.A. Res. & Tech. Support Center of Petroleos de Venezuela, S.A. (PDVSA),  
P.O. Box 76343, Caracas 1070A Venezuela*

Solid surface tension is an important parameter in wettability characterization. Although traditionally inaccessible, its evaluation is now possible using the equilibrium contact angles of three liquids of known surface tension components that is, Lifshitz-van der Waals (LW) and acid-base (AB) components. In practice, most of the very well characterized liquids spread, particularly in platinum, so no information can be obtained from them. We have generalized the proposed equations to measure surface tension components for the case of two liquids system: One of them in equilibrium surrounding the solid, and the second as a drop on top of the solid. We have applied different liquids combinations and from them evaluated the platinum surface tension components. Sometimes, the equilibrium found corresponds to that in which a film of the surrounding liquid is kept on top of the solid, this case has been treated with a modified Young equation and in this way used for surface tension components determinations.

## 216.B4 RUPTURE OF THIN WETTING FILMS ON HYDROPHOBIC SURFACES

J. Mahnke, K.W. Stöckelhuber, H.J. Schulze

*Max-Planck-Institute for Colloid and Interface Science,  
Research Group at the Freiberg University of Mining and Technology, Freiberg/Saxony, Germany*

Three elementary processes are regarded to be essential for the particle-bubble-attachment during froth flotation. A wide range of surface active reagents is used to make these processes fast and selective. Since the structure of the adsorption layers on the solid surfaces is not exactly known it is quite difficult to find correlations between their structure and their influence on the rupture of the thin wetting film.

In this paper we will present experiments made with adsorption layers with a better known structure, namely self assembled  $-\text{Si}(\text{CH}_3)_3$  layers and Langmuir Blodgett layers. In a first part we will discuss the relationship between macroscopic and microscopic contact angles (measured by droplet condensation under a microscope) and the critical thickness of the film. An energetic estimation and the common theories on hydrophobic interaction forces provide some arguments for an upper limit of  $h_{\text{crit}}$  in the range of 50-60 nm on methylated glass surfaces. The calculated parameters for the hydrophobic forces are in good agreement with SFA measurement from the literature. Measurements on Langmuir Blodgett layers are presented in the second part of the paper. Although their hydrophobicity is only slightly higher than that of completely methylated glass they show a totally different behaviour. The rupture thicknesses are in the range of 60 nm up to hundreds of nanometres and can not be interpreted only with acting long range hydrophobic forces. These experiments must rather be discussed taking into account the more complex structure of LB layers, including formation of domains and defects and structure changes in liquid media. To characterize the structures mainly phase shift interference microscopy is used. This technique provides a high resolution of 0.1 nm and a lateral resolution of 0.5  $\mu\text{m}$ . Based on experimental results and a theory developed by Sarma et al. [1] the lateral dimensions of first holes that lead to film rupture are estimated.

**217.B4****PECULIARITY OF DISPERSE MINERAL WETTING  
BY SUCROSE SOLUTIONS****V. Mank, N. Stetsenko***Institute of Biocolloidal Chemistry by National Academy of Science of Ukraine, Kiev, Ukraine,  
Ukrainian State University of Food Technologies, Kiev, Ukraine*

Wetting of porous bodies plays an important role in technological processes such as, impregnation of porous materials by various solutions and compounds, clearing of fabrics and other materials from dirt, intensification of oil and gas extraction etc. The wetting of disperse minerals is one of the important characteristics, which lets to estimate intensity of interaction of a surface of a disperse phase with liquids, making dispersional matter. We had spent systematic researches of wetting processes and of capillary impregnation some disperse minerals of Ukraine by water and sugar solutions. It is established that the capillary impregnation of mineral powders is well described by equations of liquid capillary rise, deduced for separate capillaries. The impregnation of mineral dispersions is carried out in two stages. On first there is the filling of macro and mesopores, formed between separate particles and their aggregations, and on second - diffusional penetration of a liquid in mineral micropores. At impregnation by sugar solutions it is established, that at the first stage of this process adsorption of water and some of sucrose is observed, therefore the concentration of an initial solution is increased. At the second stage water is adsorbed only. Thus, in thin pores of disperse minerals does not occur adsorption of sucrose and exists some unsolved volume. At impregnation of minerals dispersions by the sugar solutions have found out increase of a liquid quantity, which can be adsorbed in comparison with impregnation by water. On the basis of received data a hypothesis about influence raised of osmotic pressure of a sucrose solution is offered, therefore occurs deaggregation of disperse particles and increase of interpartical space.

**218.B4****GENERALISED ADHESION MAPS FOR PREDICTING THIN FILM  
TRANSITIONS IN CRUDE-OIL/BRINE/ROCK SYSTEMS****Aniello Mennella<sup>1</sup>, Steven L. Bryant<sup>2</sup>**<sup>1</sup>*Eniricerche S.p.A., S. Donato Milanese, Italy*<sup>2</sup>*TICAM, University of Texas at Austin, Austin, USA.*

Thin film transition phenomena are of special interest to the petroleum industry. After crude oil is trapped in reservoir rocks, it can alter the wettability of the rock surface, with profound implications for the transport of fluids. Even though the correlation between wetting transition and wettability alteration is qualitatively evident from many experiments, a quantitative understanding of this correlation suitable for field application requires an improved predictive tool. In this work we describe one aspect of such a tool, the generalised adhesion map, which can be useful for interpreting laboratory studies of the wetting transition.

The generalised maps are calculated from the DLVO theory of the interaction between two plane surfaces, neglecting structural forces. The double layer part of the interaction is determined from the exact solution of the non-linear Poisson-Boltzmann equation. Several sets of boundary conditions are studied.

The calculated maps are compared with literature data from adhesion test experiments and surface forces measurements. Because the choice of boundary conditions strongly influences the maps, the comparison provides some insight into which conditions may be expected to apply in natural systems. Implications of this are then discussed.

**219.B4****ADHESION OF FOOD EMULSIONS  
TO PACKAGING AND EQUIPMENT SURFACES****Marie-Caroline Michalski<sup>1</sup>, Stéphane Desobry<sup>1</sup>, Valery Babak<sup>2</sup>, and Joël Hardy<sup>1</sup>**<sup>1</sup>*Laboratoire de Physico-Chimie et Génie Alimentaires, ENSAIA-INPL,**VANDOEUVRE-LES-NANCY, France*<sup>2</sup>*INEOS-Russian Academy of Sciences, Moscow, Russia*

Adhesion of food emulsions is a problem of first importance in the recycling of packages and cleaning of industrial equipments, as well as from the consumer's point of view. We chose to measure adhesion experimentally by weighting the mass of emulsions (adhesion amount) remaining on solid surfaces after mutual contact. Surfaces of different hydrophilicity have been tested: PTFE, LDPE, PET, stainless steel and glass. The free adhesion energy of solids in contact with water ( $W_{aw}$ ), determined from contact angle measurements, varied in the range 10-140 mJ/m<sup>2</sup>. Results were checked on model emulsions using pure white vaseline oil.

It has been found that the adhesion of emulsions, stabilized by whey protein isolates or sodium caseinate and phospholipids, to solid surfaces depends primarily on their free adhesion energy ( $W_a$ ), their roughness, polarity and viscosity of dispersed and continuous phases, rheological properties of emulsions, droplet size and interfacial and surface tensions, time of contact between emulsions and solid substrates, etc.

The observed decrease of the adhesion amount of oil-in-water (o/w) emulsions with decreasing  $W_{aw}$  may be explained by the increasing hydrophilization of the outer side of protein adsorption layers formed on solid substrates. This phenomenon would be due to the conformational rearrangements of macromolecules by hiding their hydrophobic moieties in contact with hydrophobic substrates and, consequently, by decreasing adhesion forces between emulsion droplets and substrates. Moreover, in the first moments of contact, adhesion on hydrophobic surfaces may be prevented by the hydrophilicity of the continuous phase and of surfactants at water/oil interface.

Different models to calculate theoretical value of  $W_a$  were tested and compared with adhesion measurements. Models taking less acid-base properties into account were more adapted to hydrophobic products. Results were interpreted on the base of physicochemical mechanics which relates rheological and adhesional properties of emulsions to microscopic adhesion forces acting between liquid droplets and surfaces.

**220.B4****DEWETTING OF THIN POLYMER FILMS ADSORBED ON SOLID  
SUBSTRATES: A MC SIMULATION OF THE EARLY STAGES****Andrey Milchev***Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Using an off-lattice bead-spring model of flexible polymer chains containing  $N = 32$  beads under bad solvent conditions, thin films of polymer melts are simulated. The films are contained between two parallel plates, the upper plate being purely repulsive while the lower plate exerts a short range attraction on the polymer layer so that a dense thin film is adsorbed on it for large enough attraction strength  $E$ . Then "quenching" experiments are simulated by suddenly reducing  $E$  at time  $t=0$  and monitoring the time evolution of the polymer film. While for large enough final values of  $E$  only the density of the film is somewhat decreased but the film stays laterally homogeneous, for  $E$  less than a critical value  $E_C$  we observe spontaneous formation of holes in the film and it breaks into droplets. The early stages of the time evolution of this process are studied both by recording the time dependence of the adsorbed amount, the average thickness of the layer, the distribution function of the mean-square displacements of the chain segments, and with the help of snapshot pictures of the system configurations. It is found that the time evolution in the early stages of the dewetting process is governed by power laws of the time, elapsed after the quench. Also equilibrium properties of the films are investigated, including both collective properties, such as density profiles and radial distribution functions, and single-chain properties, such as parallel and perpendicular parts of mean-square gyration radii, in dependence of the adhesive strength  $E$  of the substrate.

**221.B4****MECHANISMS OF WETTING AND SPREADING OF  
"SUPERWETTERS" ON SOLID SURFACES****A. Nikolov and D. Wasan***Department of Chemical Engineering, Illinois Institute of Technology, Chicago, IL, 60616, USA.*

The spreading of trisiloxane polyoxyethylene surfactants on different types of solid surfaces was studied. Using reflected light interferometry, the three phase contact dynamic versus surfactant concentration, ethoxy chain length and humidity were monitored. Due to the low surface tension, a wedged film was formed at the three phase contact line. It was seen that as a result of the surface tension gradient, the aqueous solution spread on the solid surface and a film was formed. The film thickness stability and film tension gradient are the driving forces for the superwetting phenomenon. The film thickness stability was analyzed based on the film disjoining pressure isotherm and silicon surfactant droplets interactions with the solid/liquid and vapor/aqueous interfaces.

**222.B4****EVALUATION OF SOLIDS HYDROPHOBICITY****S.V. Pakhovchyshyn, V.F. Grytsenko, A.P. Shimansky***Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Prospekt Nauky 31 Kyiv, 252028 Ukraine*

The wetting is considered to be a process arising by contact of a solid surface with liquids and consisting in spontaneous movement of liquid along a solid surface, which is caused by gradient of chemical potential of liquid molecules at interface. For characterization of water-repellent properties of hydrophobic solids the hydrophobicity index is proposed. This index is equal to unit for hydrophobic solids, such as methyl-silica or polytetrafluorethylene (PTFE) and it is equal to zero for hydrophilic solids, such as silica or calcite. This index is determined by means of capillary impregnation of the aqueous ethanol solutions. The minimum ethanol concentration,  $C_x$ , must be determined enabling the capillary impregnation by examined powdery solid. The maximum concentrations,  $C_{max}$ , are essential for the capillary impregnation by PTFE and methyl-silica. The hydrophobicity index,  $I_{wr}$ , can be determined as:  $I_{wr} = C_x / C_{max}$ . For example,  $I_{wr}$  for thermally exfoliated graphite is equal to 0.45 against 0.23 for initial untreated graphite.

**223.B4****LIMITING VALUES OF DYNAMIC CONTACT ANGLES****Jordan G. Petrov***Institute of Biophysics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Block 21, 1113 Sofia, Bulgaria.*

Maximum velocities of wetting and dewetting of solid surfaces are achieved at the limiting values of the advancing and receding dynamic contact angles. However, molecular-kinetic theory [1] and hydrodynamic theory [2] of wetting dynamics define different dynamic contact angles and predict different maximum wetting or dewetting velocities for the same system. This discrepancy is removed when the particular definitions of dynamic contact angle are related to each other.

The rigorous definition of dynamic contact angle as a boundary condition of the differential equation describing the profile of the moving meniscus meets difficulties close to the contact line arising from the "no slip" requirement of hydrodynamics. For this reason theory of wetting dynamics usually operates with local slopes of the fluid interface whose specification is a matter of additional problems, or uses "apparent" dynamic angles which can be easily measured but become physically inconsistent when a viscous deformation exists. Instead of them we utilise the well defined "extrapolated" dynamic contact angle that serves as a boundary condition of the Laplace equation applied to the quasi-static part of a dynamic fluid interface. Dependences of  $\Theta_{ext}$  and of a specific local slope  $\Theta_{qs}$  of the fluid interface on contact line velocity, liquid viscosity, density, surface tension and static solid surface wettability are obtained for the

most general case of significant viscous, capillary and gravitational forces. These dependences show that a non-zero limiting local slope and a zero limiting extrapolated contact angle can be simultaneously achieved at the maximum dewetting velocity.

The available analytical relationships between the local slope, apparent and extrapolated dynamic contact angles in systems without gravitational effects (narrow horizontal capillaries) are also used to relate the limiting values of the dynamic contact angles. The relationships confirm the above conclusion that the apparent contradiction between the predictions of de Gennes' hydrodynamic theory [2] and Blake's molecular-kinetic theory [1] or Derjaguin's *a priori* assumption [3] is due to neglected viscous deformation in the latter cases.

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## 224.B4 DYNAMIC CONTACT ANGLE AND VISCOUS DEFORMATION OF THE FLUID INTERFACE AT A MOVING VERTICAL FLAT WALL

Peter G. Petrov and Jordan G. Petrov

Bulgarian Academy of Sciences, Institute of Biophysics, Acad. G. Bonchev St., Block 21,  
1113 Sofia, Bulgaria

A rigorous definition of dynamic contact angle for the most general case of significant capillary, viscous and gravitational force balance is considered. A dynamic meniscus at a vertical flat wall withdrawn at constant velocity from a liquid is divided into three regions: (1) a molecular region located in the immediate vicinity of the moving three-phase contact line; (2) a hydrodynamic region where viscous and capillary forces are dominant; (3) a quasi-static region located far away from the solid surface, where only gravitational and capillary forces come into play. The extrapolated dynamic contact angle,  $\theta_{\text{ext}}$ , serving as a boundary condition of Laplace equation for the quasi-static part of the fluid interface is used as a main quantity of the wetting dynamics. Its dependence on contact line velocity,  $U$ , viscosity, density, surface tension of the liquid and static wettability of the solid, is obtained and numerically analysed. The dimensions of the viscous deformation of the meniscus are specified and also related to the above material properties of the system. A nonmonotonous velocity dependence of the thickness of the viscous deformation,  $h_{\text{qs}}$ , is found.

Two different dynamic behaviours of the contact line, of constant or velocity dependent actual dynamic contact angle, are considered, and a strong difference between the corresponding dependences of  $\theta_{\text{ext}}(U)$  and  $h_{\text{qs}}(U)$  is established; velocity dependence of the actual dynamic angle makes the extrapolated dynamic angle decrease from the static value to 0 much faster and strongly reduces the viscous deformation of the moving meniscus.

## 225.B4 LAYER OF MICROPARTICLES ON A LIQUID POLYMER

Virginie Ponsinet

Laboratoire de Physique de la Matière Condensée, URA-CNRS 792, Collège de France,  
11 pl. M. Berthelot, 75005 Paris, France

We are interested in solid surfaces whose structure and possibly wetting properties can be changed by an external action: a first experimental system is a composite made of a glassy polymer layer with solid micrometer-size particles anchored at the surface. When the polymer is heated above its glass transition temperature, the particles are floating with an equilibrium position determined by the Young angle of the liquid (polymer) on the solid (particle). We study this equilibrium position, after quenching of the polymer into its glassy state, by optical and atomic force microscopy, as well as the wetting properties of the composite surface as functions of the particles surface energy, size and density.

In the case of a low surface energy polymer and high surface energy particles, we have shown that the more the particles are immersed, the smaller their effect is on the wetting properties of the surface. On the other hand, we have found possible to move ferromagnetic particles at the surface by application of a 50 T/m magnetic field gradient while the polymer is liquid, and that the wetting properties of the resulting solid surface are modified.

## **226.B4 EFFECT OF EVAPORATION ON IMBIBITION: COMPOSITE MENISCI**

**H.M. Princen**

*Mobil Technology Company, Paulsboro Technical Center, Strategic Research Center, Paulsboro,  
New Jersey 08066, USA*

Motivated by an unexpected result of certain imbibition experiments, we have analyzed the effect of evaporation from a brine-filled, strongly water-wet porous solid whose lower end is brought into contact with bulk oil. The surprising finding was that, after sometime, oil imbibed into the core. This could imply that the core was in fact "mixed wet", were it not for the fact that the experiment was carried out in the open atmosphere, i.e., without exclusion of evaporation of water from the core. Using the simple model of a cylindrical capillary, we show that imbibition of oil is the natural consequence of such evaporation. As part of this study, we have analyzed in detail the shape and properties of "composite menisci" where oil, air and water all meet in the later stages of the evaporation process. Such menisci are expected to be common in natural gas/crude oil/ brine and other systems.

## **227.B4 INFLUENCE OF MOLECULAR ORDERING ON THE WETTING/DEWETTING BEHAVIOR OF ULTRATHIN ALKANE FILMS AT SILICON DIOXIDE/AIR INTERFACES**

**H. Riegler, T. Pfohl, and C. Merkl**

*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5,  
D-12489 Berlin, Germany*

Ultrathin films of alkanes of various chain lengths at  $\text{SiO}_2$ /vapor interfaces have been used to investigate the influence of short and long range forces on the wetting behaviour. For certain alkane chain lengths surface freezing effects at the alkane/substrate interface cause three different wetting topologies: Below the bulk freezing temperature a Stranski-Krastanov-like topology, between the bulk and surface (alkane/silicon dioxide) freezing temperature pseudo-partial, and above nearly complete wetting is observed. Systematic studies of the wetting behaviour of different types of shape-anisotropic molecules (unpolar, slightly polar, polar (amphiphiles)) reveal general relations between local interactions, the molecular ordering at interfaces, and the (typical) autophobic behavior of such molecules.

C. Merkl, T. Pfohl, and H. Riegler, *Phys. Rev. Lett.*, submitted.

## **228.B4 MOLECULAR ADHESION INTERACTIONS BETWEEN LANGMUIR MONOLAYERS AND SOLID SUBSTRATES**

**Hans Riegler and Karlheinz Graf**

*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5,  
D-12489 Berlin, Germany*

Substrate/monolayer adhesion interactions between differently prepared  $\text{SiO}_2$  surfaces and different Langmuir monolayers were investigated. From the relation between the contact angle and the surface tension of a Langmuir monolayer in the configuration of Langmuir wetting the work of adhesion between

the substrate and the monolayer as a function of the molecular packing and the transfer ratios were determined. Thus the *molecular* work of adhesion of substrate/monolayers was quantified. The relation between the local adhesion interactions and the molecular packing and structure is presented and substrate-induced phase transitions are discussed. The comparison of the contact angle behaviour of different monolayers unambiguously proves the invalidity of the Neumann EQS approach. Dynamic contact angle measurements allow the determination of the density of the adhesion binding sites.

K.-H. Graf and H. Riegler, *J. Coll. Surf.*, in print.

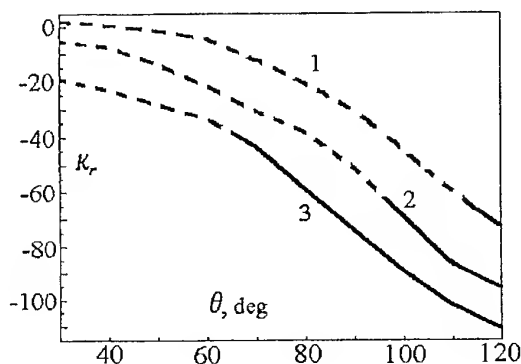
## 229.B4 EVALUATION OF THE SPECIFIC EXCESS FREE ENERGY OF THE REGULAR WETTING PARAMETER ON THE BASIS OF THE THERMODYNAMIC PERTURBATION THEORY

V.M. Samsonov, A.V. Lebedev, L.M. Shcherbakov  
Tver State University, 170000, Tver, Russia

Experimental measurements of the line tension  $k$  of the triple line (in the system droplet-solid-gas) has proven very difficult. But obviously, the fact is that  $k$  can take both sign and its absolute value  $\leq 10^{-9}$  N [1]. It was shown [2] that  $k$  should be the product of a typical surface tension of liquid  $\sigma$  and a characteristic correlation length. In [3] on the basis of a similarity approach we have shown that the reduced line tension  $k_r = k\sigma/a$  of the equilibrium rectilinear triple line ( $a$  is an effective molecular diameter) should be universal function of the equilibrium contact angle ( $\theta_e^\infty$ ):

$$k_r = F(\cos \theta_e^\infty) \quad (1)$$

Derivation [3] of (1) is correct only for the case when  $T \ll T_w \approx T_c$ , where  $T_w$  is the temperature of the wetting transition,  $T_c$  is the critical temperature of liquid. The above conclusion on the universality of the function  $F$  can be justified via direct calculations of  $k_r$ . In frames of the thermodynamic perturbation theory, the excess free energy  $\psi$  of the system under consideration will be equal to the mean excess potential energy  $\langle \Delta U \rangle$  calculated for the unperturbed Gibbs distribution (our choice of the reference system corresponds to the bulk liquid phase). The results of computer calculations of  $k_r$  versus the contact angle  $\theta$  for spherical cap droplets of Lennard-Jones (L.-J.) single component liquids are presented in Fig. Curves 1-3 correspond to different values of the simplex  $\epsilon_r = \epsilon_s/\epsilon_l$  (0.5, 2 and 5), and, respectively, of  $\theta_e^\infty$  (110°, 90° and 60°). Here  $\epsilon_l$  is the energetic parameter of the pair potential for liquid,  $\epsilon_s$  is the corresponding effective value for the solid ( $\epsilon_s$  will be the usual energetic parameter of the potential for a L.-J. solid). The beginnings of the solid lines correspond to the equilibrium values of  $\theta$  and  $k_r$ . One can see that the equilibrium values of  $k_r$  are poorly dependent on  $\theta_e^\infty$  ( $-60 \leq k_r \leq -40$  when  $\theta_e^\infty$  varies from 110° to 60°). So, the Eq.(1) has been justified.



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## 230.B4

MONTE-CARLO COMPUTER SIMULATION  
OF THE PRIMARY ACT OF WETTING

V.M. Samsonov, A.V. Lebedev, S.D. Muravyev  
Tver State University, 170000, Tver, Russia

Two variants of the Monte-Carlo method are approbated and discussed: 1) a new mesoscopic approach based on division a macroscopic droplet under consideration (of order of 1 mm in size) into small in comparison with its volume cells; 2) usual dynamic version. One of the goals of the mesoscopic simulation is to confirm based on the H-theorem (the free energy decreasing principle) conclusion about the principal role of the sign of the wetting perimeter line tension in the primary act of wetting [1]. The results of simulation demonstrate an apparent fractal structure of the triple line region (Fig. 1). Contrary to the above method, usual simulation approach is suitable to investigate the spreading mechanisms on molecular level. Fig. 2 represents the MC trajectories for a microdrop of simple liquid ( $R_0=3a$ , where  $R_0$  is the initial droplet radius and  $a$  is an effective molecular size). The trajectories demonstrate some oscillating slip displacements of molecules along the substrate, however, in general the "rolling motion" macroscopic mechanism [2] is more adequate. After short region  $r \propto t$  (Fig. 3)  $r$  follows to the diffusional temporary law  $r \propto t^{0.5}$  that is in accordance with the experimental data [3]. The configuration after 10000 steps is shown in Fig. 4.

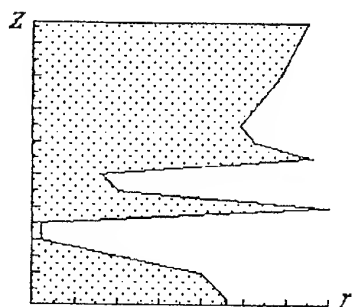


Fig. 1.

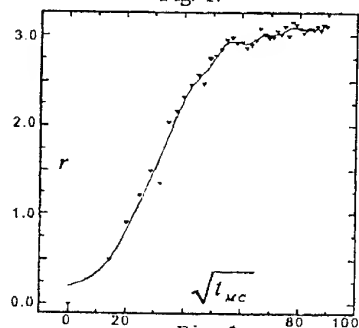


Fig. 3.



Fig. 2.

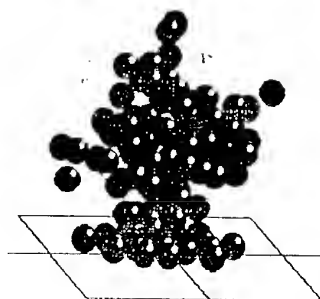


Fig. 4.

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## 231.B4

## TOPOLOGIC CONCEPT OF WETTING FILMS

Viadimir Smorodin

*Inst. Tecnologia Quimica e Biologica, R. Quanta Grande, Apt. 127, P-2780, Oeiras, Portugal;  
Department of Chemistry, Lomonosov State University, Moscow 119899, Russia*

In accordance with Derjaguin's ("structural") concept of wetting films, unusual dependencies of intensive properties of wetting films (or boundary layers) on their thickness are expressed with a so-called a

"disjoining" pressure (including a "structural" component). In this approach the films were treated as continuous and stable structures [1].

A new "topologic" approach to wetting films to have been stimulated with Derjaguin's concept is based on two main facts (eliminated in the "structural" concept): (a) effects of thermo- and hydrodynamic instabilities of films at some critical thickness, and (b) a surface heterogeneity of solids.

Taking into account these important aspects, we have analysed fourth empirical fundamentals of the "structural" concept [2]: (1) S-isotherms of the water (or polar liquids) adsorption, (2) an abnormal shear viscosity of wetting films, (3) a changed enthalpy of films, and (4) dependencies of intensive physical properties of films (including a dielectric permittivity) on its thickness [3-6].

It is found that all these phenomena can be alternately explained taking into account a surface heterogeneity of solids, changing of the film topology (during its growing or thinning) and dependencies of effective properties of films on their topologic structure.

As new heuristic consequences of the "topologic" approach were advanced: (1) a "percolational" concept of electrokinetic potential, (2) theory of electro-, thermo-, reverse osmosis and ultrafiltration through heterophilic membranes, (3) theory of heterogeneous nucleation on mixed aerosol particles, (4) new theoretical concepts of such phenomena as a microflotation and hydrophobic interactions of colloid particles [7-8].

The new "topologic" concept and the "structural" one of films in some cases may be complementary and be united in a generalized "structural-topologic" approach [5]. But in principle, some previous empirical results should be re-interpreted, as well as new experiments can be conducted for to reach a clear truth and distinguish between the areas of validity of both approaches.

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## 232.B4

### THREE-PHASE CONTACT LINE EXPANSION ON THE SURFACE OF FINE PARTICLES

H. Stechemesser<sup>1</sup>, A. Nguyen-Van<sup>2</sup>, G. Zobel<sup>1</sup>

<sup>1</sup>Max-Planck-Institute for Colloids and Interfaces,

Research Group at the University of Mining and Technology, Freiberg, Germany

<sup>2</sup>Ian Wark Research Institute, University of South Australia, The Levels, Australia

Expansion of the three-phase (solid-liquid-gas) contact line (tpcl) on the surface of silanated sphere as a consequence of the solid sphere against an initially planar air-liquid interface was experimentally studied by means of CCD high-speed technique.

The air-liquid interface is formed at the bottom of a capillary tube (of diameter of 1 cm) which is filled with desired solution. A solid particle (250-350  $\mu\text{m}$ ) settles down in the solution and interacts with the air-liquid interface. The tpcl expansion is microscopically observed beneath the air-liquid interface in the direction rectangular to the tpcl planes. The kinetics of the expansion is measured with a CCD high-speed camera (1000 frames per sec.), through the objective of an inverse microscope.

The instantaneous patterns of the three-phase contact line are then digitalized and processed.

The dependence of the central angle (measured at the particle centre) of the contact line on time was determined and theoretically simulated. Results of this simulation indicated that the molecular-kinetic theory best describes the dynamics of tpcl expansion and that the line tension causes a strong effect on the tpcl expansion (dewetting). The measured value of line tension for silanated glass surfaces is of order of  $10^{-6}$  to  $10^{-7}$  Newton and positive.

It is expected that these results provide a fundamental information toward the better understanding the theory of flotation.

## 233.B4

### SUPERFICIAL AND WETTING TRANSITIONS IN DILUTE TRISILOXANE SURFACTANTS AQUEOUS SOLUTIONS

T. Svitova<sup>1</sup>, R.M. Hill<sup>2</sup>, C.J. Radke<sup>3</sup>, G. Yakubov<sup>1</sup>

<sup>1</sup> *Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia*

<sup>2</sup> *Dow Corning Corp., Midland, Michigan, USA*

<sup>3</sup> *University of California at Berkeley, Berkeley, USA*

According to Cahn, in any mixture of two fluid phases close to their critical point, contact angles become zero against a surface of any third phase which is not involved in the critical point. The nonionic surfactants-water systems, having two critical consolute points and showing large variety of coexisting liquid phases, as it was shown by many authors, are very good candidates for critical wetting behavior studies. The trisiloxane nonionic surfactants, known as superspreading agents, are able to enhance water spreading over low energy surfaces like paraffin and polyethylene, thus being of special interest. Equilibrium interfacial properties and wetting behavior of aqueous solutions of three nonionic trisiloxane surfactants BE- $n$ (B-(Me<sub>3</sub>SiO)<sub>2</sub>Si(Me)(CH<sub>2</sub>)<sub>3</sub> - hydrophobic moiety, the same for surfactants studied,  $n=6, 8$  and 12, ethoxy-group number) were studied in the dilute region near the critical aggregation concentration (CAC), and up to 0.5 % wt. at constant temperature 22°C. BE-6 and BE-8 form vesicles at the CAC while BE-12 forms micelles. It was found that the tension isotherms have S-like shape, namely, tension being almost constant in the concentration range from 1 to about 5 times the CAC and significantly decreasing above this range. The turbidity of BE-6 and BE-8 solutions progressively increases at the concentration above 5-7xCAC, which is related to formation of a new phase in the solution. Turbidity of BE-12 solutions is very low up to at least 5 wt %, and no bulk phase transition was observed for this surfactant. Contact angle measurements of these solutions on Parafilm (paraffin wax film) have shown that the transition from partial wetting with low but measurable contact angles to complete wetting ( $\cos\theta=1$ ) occurs at the concentrations significantly above CAC and surface tension about 21 mN/m, that is noticeably lower than Parafilm critical wetting tension (25 mN/m), obtained by pure liquids wetting studies. Note that critical wetting concentration rises with surfactant ethoxy-chain length increase. These transitions correspond to the second region of the interfacial tension downfall. At the same concentration region the equilibrium spreading coefficient for solution/tetradecane becomes positive and a transition from a lens to a rapidly spreading unstable thick film was observed for these solutions on tetradecane. Dynamic surface and interfacial tension measurements have shown that the observed transition from "low" to "high" adsorption is accompanied by significant increases of surfactant adsorption rates at both the air/water and oil/water interfaces. Thus, for BE-6 and BE-8 systems the transition to perfect wetting could be related to the possibility that these systems are consisting of two liquid phase, one of which has lower surface and interfacial tension. For BE-12 containing systems so-called pre-wetting transition occurs, i.e. a sudden perfect wetting by a phase though not existing into a bulk solution but arising at the interfaces that is promoted by the contact with the low energy surfaces. The superficial phase transition in this case is proposed to be caused by preferential accumulation of the most surface-active homologs with short ethoxy chains at the low energy surfaces.

## 234.B4 CAPILLARY WETTING IN SILANIZED SILICA FIBROUS ASSEMBLIES

Mieko Tagawa<sup>1</sup>, Keiko Gotoh<sup>2</sup> and Yoshiko Nakagawa<sup>1</sup>

<sup>1</sup> *Nara Women's University, Kita-Uoya-Higashi-machi, Nara 630, Japan*

<sup>2</sup> *Kyoto University of Education, 1 Fukakusa-Fujinomori-cho, Fushimi-ku, Kyoto 612, Japan*

The spontaneous penetration of wetting liquids into porous materials due to capillary action is important in a wide range of technological fields. We determined capillary wetting rates in silanized silica fibrous assemblies by water/ethanol mixtures from changes in the electric conductivity due to wetting.

Silica filters commercially available were used as silica fibrous assemblies. The filters have a pore diameter of ca. 0.3  $\mu\text{m}$  and the thickness of 0.8 mm. For contact angle measurements, fibrous silica having diameter of 50-100  $\mu\text{m}$  was used for experimental convenience. These were purified by extraction with water, ethanol and ethyl ether, and were modified with  $\gamma$ -aminopropyltriethoxysilane (APTES) and methyltriethoxy-silane (MTES). Water/ethanol mixtures having different volume ratios were chosen as wetting liquids ( $[\text{KCl}] = 1 \times 10^{-3} \text{ mol/dm}^3$ ).

The capillary wetting rate were measured using a newly developed apparatus. The circular silica filters were horizontally packed in a cylindrical polytetrafluoroethylene cell. The platinum electrodes with tiny holes were attached to the top and bottom faces of the plug. The head of the wetting liquid was adjusted to the bottom level of the plug and then the change in the electric conductivity,  $\lambda$ , with time,  $t$ , was recorded. The advancing contact angle of wetting liquid on silanized silica were measured by the Wilhelmy method using an electrobalance and a reversible elevator.

The electric conductivity began to increase at  $t=t_o$  and reached a constant value,  $\lambda_c$ , at  $t>t_c$ . The  $t_o$  and  $t_c$  correspond to the times when the wetting liquid full up the shortest capillary and all capillaries in the assembly, respectively. Since the present systems are all identical in the capillary distribution,  $t_o$  can be used as a measure of the capillary wetting rate. The values of  $t_o$  for the untreated and APTES-treated silica fibrous assemblies increased with increasing volume ratio of ethanol, indicating that the addition of ethanol to water reduced the wetting rate. In the case of MTES-treated silica fibrous assembly, the capillary wetting was observed above 30% of volume ratio of ethanol, and  $t_o$  decreased with increasing volume ratio of ethanol. The advancing contact angle of the wetting liquid decreased with increasing volume ratio of ethanol for untreated and silanized silica. In the region of 0 to 50% of ethanol, the order of magnitude of the angles was MTES-treated silica > APTES-treated silica > untreated silica.

According to Washburn's equation, it is derived that  $1/t_o$  is proportional to  $\gamma \cos \theta / \eta$  ( $\gamma$ : surface free energy of wetting liquid,  $\theta$ : advancing contact angle,  $\eta$ : viscosity of wetting liquid) when gravitational acceleration is negligible compared to capillary force. Therefore,  $1/t_o$  was plotted against  $\gamma \cos \theta / \eta$  using the experimental data of  $t_o$  and  $\theta$ . The value of  $1/t_o$  increased with increasing  $\gamma \cos \theta / \eta$ . The results for untreated silica in the region of 0- 10% ethanol concentration deviated from the other results. This suggests that liquid viscosity in the vicinity of the hydrophilic silica surface is larger than that in bulk.

## 235.B4

### PARTICLE ADHESION TO SILANIZED SILICA IN WATER/ETHANOL MIXTURES

Junko Tao<sup>1</sup>, Keiko Gotoh<sup>1</sup> and Mieko Tagawa<sup>2</sup>

<sup>1</sup>Kyoto University of Education, 1 Fakakusa-Fujinomori-cho, Fushimi-ku, Kyoto 612, Japan

<sup>2</sup>Nara Women's University, Kita-Uoya-Higashi-machi, Nara 630, Japan

Particle adhesion is a fundamental subject which has various industrial applications. In the present study, we investigated adhesion of polymer particles to silanized silica in water/n-alcohol mixtures. The experimental results were discussed in terms of surface free energies and electrokinetic potentials.

Spherical particles of polyethylene and nylon used have mean diameters of 4 and 5  $\mu\text{m}$ , respectively. Silica plates were used as substrates in particle adhesion experiments. Contact angle and electrokinetic potential measurements were carried out using fibers for experimental convenience. Silica was modified with  $\gamma$ -aminopropyltriethoxysilane (APTES), methyltriethoxysilane (MTES) and perfluoroethyltrimethoxy-silane (FETMS). Methanol, ethanol, propanol and butanol of extra pure grade and doubly distilled water were used as media.

Polyethylene or nylon particles were dispersed in water/n-alcohol mixtures containing  $1 \times 10^{-3} \text{ mol/dm}^3$  of potassium chloride. The silica plate was perpendicularly immersed in the dispersion. After immersion of 60 min, the number of particles adhering to the plate was counted using a microscope. The particle adhesion was expressed as the average number of particles per  $\text{mm}^2$ ,  $n_a$ . The electrokinetic potentials of the particles and substrates in water/ethanol mixtures were measured by the streaming potential method. The dispersive and nondispersive components of surface free energies of the particles, substrates and liquids were determined by contact angle measurements employing the Wilhelmy method.

The particle adhesion was enhanced by the silanization of silica. Although there was a difference in  $n_a$  between different kinds of particles and substrates, the values of  $n_a$  decreased with increasing volume ratio of ethanol in all cases. In the polyethylene particles/MTES-treated silica system, the  $n_a$  values decreased with increasing volume ratio of n-alcohol and this tendency was noticeable in large number of carbon atoms of n-alcohol. From the electrokinetic potential measurements, APTES-treated silica was found to be positively charged and the other substrates and the particles negatively charged. In all cases, the absolute values of the electrokinetic potential decreased with increasing volume ratio of ethanol. The nondispersive component of the surface free energy reduced by the silanization of silica. The dispersive surface free energies of water/ethanol mixtures were not dependent on n-alcohol concentration, whereas the nondispersive one decreased with increasing volume ratio of alcohol.

The free energy change in particle adhesion,  $\Delta G$ , was calculated from the experimentally determined dispersive and nondispersive surface free energies. The plots of  $n_a$  against  $\Delta G$  were on the same line except the results for positively charged APTES-treated silica, which lay upper the line. We experimentally determined the Lifshitz-van der Waals and acid-base components of surface free energy and related particle adhesion with the components. Conclusively, the van der Waals, hydrogen bond and electrostatic interactions relate to the particle adhesion in the present systems.

## 236.B4 IMPACTING DROPLETS OF AN EMULSION OR SURFACTANT SOLUTION ON SOLID SUBSTRATES

M. Vignes-Adler, B. Prunet-Foch, F. Legay, N. Mourougou

*Laboratoire des Phénomènes de Transport dans les Mélanges du CNRS, 4ter, Route des Gardes,  
F 92190 Meudon, France*

Coating of solid surfaces with uniform, thin liquid films occurs in many industrial processes. A common process consists of spraying some liquids or emulsions on a freshly created solid surface. In this context we have investigated the impact of a single drop of various emulsions and surface-active solutions on a solid substrate using a high speed fluorescent visualization technique. Whatever the materials in presence, the drop spreads and then retracts under the action of inertia and of capillarity respectively. Inertia induces spreading and generates a peripheral rim which is unstable to fingering. Then contact line instabilities appear under the form of festoons with pure liquids; they are damped with surface-active solutions and amplified with emulsions. Before impact the drop is spherical and its surface is minimal. When the drop reaches its maximum diameter on the surface, it looks like a flat pancake; hence, its surface increases drastically in a few ms. The corresponding surface dilational maximum rates  $\lambda_{\max}$  range between 250 and 600  $s^{-1}$ . It induces a rapid and large increase of the surface tension because surfactants have insufficient time to adsorb at the liquid-vapor interface. The dynamic surface tension has been measured by the maximum bubble pressure method and it was proved that the retraction phase is ruled by the adsorption kinetics of the surfactant. On a smooth, low surface-energy solid substrate, if the adsorption kinetics of the surfactant is slow, the dynamic surface tension is high compared to the equilibrium value and the drop may bounce back. This occurs when the coating of the surface is miscible with the organic part of the emulsion.

## 237.B4 THE FORCES OPERATIVE DURING THE FILM FORMATION FROM LATEXES

Marcel Visschers, Jozua Laven, Rob van der Linde

*Laboratory of Coatings Technology, Faculty of Chemical Engineering,  
Eindhoven University of Technology, P.O. Box 513, 5600 MB, The Netherlands*

Film formation from latexes can be composed of different physical stages: water evaporation, particle deformation and polymer chain diffusion. The particle deformation is crucial to the requirement of good final film properties. The basic theory concerning particle deformation has proved not to be successful in explaining and in quantitatively predicting 'dry' film formation, elastic modules' dependency and particle

size dependency. According to basic theories, the driving force for particle deformation is the capillary force due to the receding water/air interface.

As an indication of which forces are relevant to particle deformation, we present an overview of the estimates of the various forces operative during film formation. These forces comprise the Van der Waals force, the electrostatic repulsion force, the capillary force due to receding water/air interface and the capillary force due to the presence of so called 'liquid bridges'. Our calculations show that only the receding water/air interface and the liquid bridges can supply the force needed for the particle deformation. Furthermore, these two capillary forces explain the phenomenon of dry film formation as observed by, among others, Sperry et al.

Apart from the driving force for film formation, the mechanical behaviour of the polymer particles is of importance. Basic theory has assumed them to be elastic, while there is strong experimental evidence them to be visco-elastic. The elastic behaviour and both the capillary forces are combined in a criterion for the maximum admissible shear modulus admissible for particle deformation. The case of viscoelastic behaviour and liquid bridges is also examined.

Our calculations on liquid bridges reveal that the capillary force due to these bridges is almost independent of the relative air humidity except very close to 100% humidity. Concerning the force due to a receding interface, the Mason-Brown expression has been extended to include the surface force and the degree of deformation. An incorporation of visco-elasticity, Van der Waals forces and both capillary forces will in future lead to a successful description of the particle deformation.

## 238.B4 THE MEASUREMENT OF THE CAPILLARY PRESSURE IN PACKED BEDS OF POLYSTYRENE PARTICLES BY IMBIBITION

Marcel Visschers, Renno Langerlaert, Jozua Laven, Rob van der Linde

*Laboratory of Coatings Technology, Faculty of Chemical Engineering,  
Eindhoven University of Technology, P.O. Box 513, 5600 MB, The Netherlands*

Imbibition of a wet packed bed consists of the displacement of water by air. The concave curved water/air interface results in a lowering of the pressure at the water side of the interface. In order to displace water by air one must apply an external pressure across the bed to compensate for the capillary pressure. The external pressure at which water displacement just occurs, equals the capillary pressure. The capillary pressure is given by  $12.9\sigma_{w/a} \cdot \cos\alpha \cdot r_p^{-1}$  where  $\sigma_{w/a}$  is the water/air surface tension,  $\alpha$  the contact angle and  $r_p$  the particle radius.

The packed bed consists of monodisperse, submicron polystyrene particles. The bed is prepared using an ultracentrifuge. In order to characterise the bed we have performed permeability measurements. The measured permeability is by a factor 100 larger than that obtained by using the Blake-Kozeny equation.

The capillary pressure of a packed bed amounted to values among 0.2 and 3 atm. in the case of surfactant-free water. According to the Laplace equation, the capillary pressure should amount to 26 atm. in the case of 700 nm particles, and a  $0^\circ$  contact angle. The difference between these values may be caused by the hydrophobicity of the polystyrene particles; a contact angle close to  $90^\circ$  results in a value for the capillary pressure as found by our imbibition measurements. We will also show results with systems to which a surfactant was added.

At external pressures exceeding the capillary pressure air breakthrough occurs suggesting the existence of cracks in the packed bed: channelling. This phenomenon is not as severe when using an specially designed air inlet. The occurrence of cracks during imbibition may severely lower the measured capillary pressure.

## 239.B4

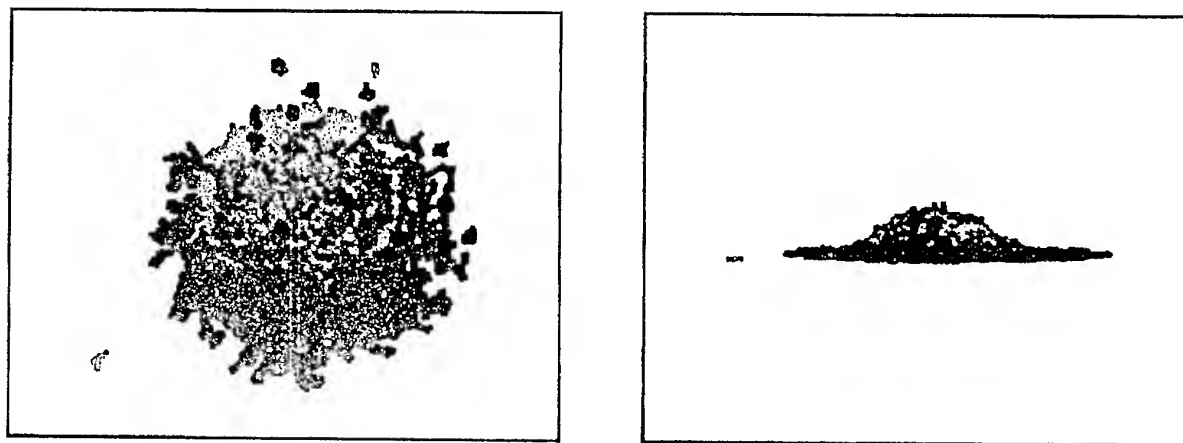
COMPLETE WETTING OF POLYMER-LIKE LIQUIDS  
BY MOLECULAR DYNAMICSM. Voué<sup>1</sup>, S. Rovillard<sup>1</sup>, J. De Coninck<sup>1</sup>, M.P. Valignat<sup>2</sup>, S. Villette<sup>2</sup> and A.M. Cazabat<sup>2</sup><sup>1</sup>Modélisation Moléculaire, Université de Mons-Hainaut, Mons, Belgium<sup>2</sup>Physique de la Matière Condensée, Collège de France, Paris, France

In wetting science, most of the recent experimental studies, computer simulations and theoretical models have been devoted to the spreading of pure polymeric liquids. Mixtures of polymers or asymmetric surface interactions for the ends of the liquid molecules have only been addressed in few studies although the problem of covering a solid substrate by a mixture of polymers is of prime importance from a practical point of view because the substrate will usually favor one of the mixture constituents.

The main features arising from the studies of one-component polymeric liquids on top of solid substrates is the "terraced spreading" phenomenon which, under well defined conditions, leads to the formation of layers of molecular thickness. High resolution ellipsometric measurements have initially brought experimental evidences of that phenomenon. The first attempt to describe its origin is due to de Gennes and Cazabat where the spreading is described as a competition between the driving force, which is due to the wall attraction, and the friction between layers of liquid and with the solid. Assuming essentially the viscous nature of the friction forces, these authors were able to recover most of the experimental observations. Among these experimental observations, the "diffusive" nature of the spreading, i.e. the growth of the radius associated to the first layer behaves as  $t^{1/2}$  should be pointed out.

Using Molecular Simulations (MD) techniques, De Coninck and coworkers could recover both the "terraced spreading" phenomenon and the  $t^{1/2}$  law. The microscopic details of the mechanism of spreading and, in particular, the role of the friction at the microscopic level, were recently also investigated using MD simulations. The results of that study were in agreement with experimental evidences and supported the validity of the de Gennes-Cazabat model based on driven force/friction competition mechanism.

In this communication, we will review the results concerning the complete wetting applied to 1-component liquid-like polymers. We will present new experimental results. Our MD approach will be extended to the case of 2-components fluids in such a way that MD simulations results for inter- and intra-molecular asymmetric interactions will be compared to experimental results respectively for mixtures of polymers and surfactant-like. Especially, the rate of covering of the substrate by the polymers, the demixing phenomenon which should occur when one of the mixture components satisfy conditions for partial wetting regime, the distribution functions in the first layer and in the direction perpendicular to the substrate will be discussed.



Fingering phenomenon during the spreading of a droplet composed of 800 16-atoms chains (red) and 1600 8-atoms chains (blue). (Left: Top view; Right: Front view)

## 240.B4 THE WETTING BEHAVIOUR OF CARBOHYDRATE MODIFIED SILICON SURFACTANTS ON PERFLUORINATED SOLID SURFACES- COMPETITION BETWEEN THE SOLID/LIQUID AND LIQUID/VAPOUR INTERFACES

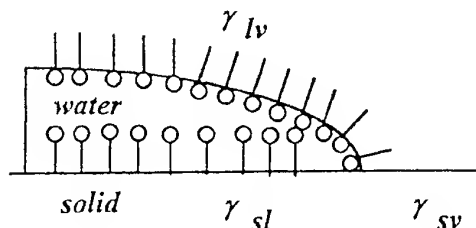
R. Wagner<sup>1</sup>, Y. Wu<sup>1</sup>, L. Richter<sup>1</sup>, S. Siegel<sup>1</sup>, J. Weismüller<sup>2</sup>, J. Reinert<sup>1</sup>

<sup>1</sup>Max-Planck-Institute for Colloids and Interfaces, Rudower Chaussee 5, 12489 Berlin

<sup>2</sup>Bayer AG, Business Sector Agrochemicals, 40789 Monheim, Alfred-Nobel-Str. 50

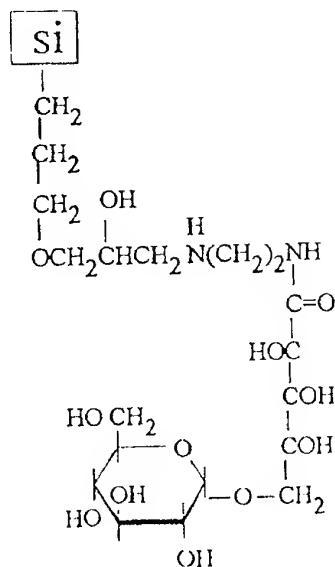
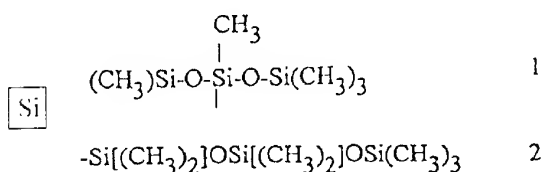
The macroscopic contact angle of a surfactant solution drop on a solid surface is determined by the power balance between the interfacial tension solid/vapour ( $\gamma_{sv}$ , constant for a given surface), the interfacial tension liquid/vapour ( $\gamma_{lv}$ , surface tension) and the interfacial tension solid/liquid ( $\gamma_{sl}$ ).

It has been shown recently that for siloxane surfactant solutions above the critical micell formation concentration (cmc)  $\gamma_{lv}$  and  $\gamma_{sl}$  develop independently because they react individually on defined surfactant structure changes.



Dependence of the interfacial properties on the siloxane structure ( $c > \text{cmc}$ )

No	$\gamma_{lv}$ (mN/m)	$\gamma_{lv}^{LW}$ (mN/m)	$\gamma_{sl}$ (mN/m)	$\gamma_{sl}^{LW}$ (mN/m)	$\Theta$ (deg)
1	21.5	19.0	2.4	0	40
2	22.2	21.0	1.2	0.06	37



For selected carbohydrate modified Si-surfactants the  $\gamma_{lv}$  and  $\gamma_{sl}$  measurements have been extended on concentrations below the cmc where a complete surface coverage can not be expected. The  $\gamma_{lv}/\log c$  and  $\gamma_{sl}/\log c$  isotherms obtained will be discussed in terms of the underlying long range (Lifshitz-van der Waals) and short range (donor-acceptor) forces. The question whether there is a surfactant structure dependent preferential adsorption on the solid-liquid or liquid-vapour interface will be dealt with on selected examples.



## 241.B4 THE TIME DESTRUCTION OF THE SEDIMENT COLUMN AS A METHOD FOR STUDY OF THE DISPERSION SYSTEM

Wiesław Wójcik<sup>1</sup>, Bronisław Janczuk<sup>1</sup>, Jose Morales Bruque<sup>2</sup>

<sup>1</sup>*Department of Physical Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq.3, 20 - 031 Lublin Poland*

<sup>2</sup>*Departamento de Física, Universidad de Extremadura, 060 71 - Badajoz, Spain.*

In our laboratory in the sixties a simple device was used to measure the time of the sediment column destruction that is proportional to the attachment forces between mineral grains. It has been found that each mineral has a particular size of its grains for which the gravitational forces are balanced by the surface forces and then the sediment column is stable. The diameter of such grains is named as "critical diameter". Using these simple device measurements of the time of the sediment column destruction of coal grains precovered with different thickness of films of n-alkanes and n-alcohols were carried out. The measurements were conducted for different size fractions of coal grains precovered with a film which thickness was changed from 0 to 8 statistical monolayers. It was found that the time of the sediment column destruction of coal grains increased with increasing film thickness, reaching constant values of the time for the films which thickness was bigger than 3-4 statistical monolayers. The destruction time also increased as the number of carbon atoms in the hydrocarbon chain of the liquids increased.

The dependences of the reciprocal of the destruction time as a function of the diameter of the coal grains are linear, and by extrapolating of these linear dependences to time equal infinity we determined the critical diameter of coal grains. The critical diameter was also calculated from a suitable equation for these straight linear dependences. The obtained results show us that the critical diameter values do not depend on the length of the hydrocarbon chains and the thickness of the films. To explain these results, the free interaction energy of molecules with coal surface was calculated. We have found that the calculated values of the free interaction energy per molecule are straight linear dependences as a function of the reciprocal of the destruction time. These straight linear dependences indicate that probably a different size of the contact plane between coal grains causes the observed changes of the destruction time.

Unfortunately, these findings do not explain all results obtained. One of them is the physical meaning of the constants in the straight linear equation between the reciprocal of the destruction time and the diameter of the grains. To solve this problem we tried to correlate the constants with some physicochemical properties of the studied liquids.

## 242.B5 EXPERIMENTAL STRATEGIES TO DETERMINE LINE TENSION

A. Amirfazli, P. Chen, S.S. Susnar, D.Y. Kwok, A.W. Neumann

*Department of Mechanical Engineering, University of Toronto, Toronto, Canada, M5S 3G8*

Line tension is a well defined thermodynamic concept; however, there is no general consensus with regard to its magnitude or sign. Experimental absolute values for line tension range anywhere from  $10^{-11}$  to  $10^{-5}$  J/m. There is no *a priori* reason to reject any of these reported values; however, it is unlikely that line tension could range over several orders of magnitude for energetically comparable systems. In this paper, to estimate the line tension, three different experimental configurations have been used as follows.

One of the direct ways of measuring line tension takes advantage of the dependence of the contact angle on the radius of the curvature for the three-phase line of a sessile drop on a solid surface. According to the modified Young equation, which includes the line tension term, a positive line tension tends to increase the contact angle as the contact radius for a sessile drop decreases. We have conducted studies on carefully prepared solid substrates using Self Assembled Monolayer (SAM) techniques and also FC-721 and DDOA surfaces, by means of Axisymmetric Drop Shape Analysis (ADSA). The line tension values obtained for various liquids are positive and in the range of  $0.8-5 \times 10^{-6}$  J/m.

To estimate the line tension by an independent second method, we have considered a heterogeneous solid surface consisting of alternating hydrophobic and hydrophilic strips. When such a surface comes into contact with a liquid in the vertical capillary rise configuration, the contact line will assume a wavy pattern. Solving the Laplace equation numerically in conjunction with the modified Young equation for this system,

we can obtain a series of computed contact line profiles representing different values of line tension. In the limits, an infinitely large line tension will result in a straight contact line, and a zero line tension results in the maximum amplitude of the wavy contact line. Line tension is then determined by finding the best computed contact line profile which overlays the experimental contact line. Fabricating such a surface consisting of alternating narrow strips using SAM techniques and experimenting with a single liquid, we obtained a line tension near  $1 \times 10^{-6}$  J/m, in agreement with the first method.

The interference of roughness and heterogeneity in determining line tension is expected to be absent in liquid lens systems. In a third method, we used the quadrilateral relation that is applicable to liquid lens systems to estimate the line tension. The quadrilateral relation is a generalization of classical Neumann triangle including line tension related terms. Using this relationship and measuring two of the three contact angles in the liquid lens system, and knowing the diameter of the lens, one can find the line tension. In our experiments, the contact angles and the lens diameter are measured using image processing schemes. For the dodecane/water/air system studied, the line tension values are negative and in the range from  $-1 \times 10^{-6}$  to  $-4 \times 10^{-6}$  J/m. The values were found to be independent of the lens size (1-7mm).

None of these measurements can be easily reconciled with the idea of a line tension orders of magnitude closer to zero.

## 243.B5

### DROPLET SPREADING: THEORY AND EXPERIMENTS

T. Blake<sup>1</sup>, A. Clarke<sup>1</sup>, A. Rankin<sup>1</sup>, J. De Coninck<sup>2</sup>, M. J. De Ruijter<sup>2</sup>

<sup>1</sup>Kodak European Research, Kodak Limited, Harrow HA1 4TY, U.K.

<sup>2</sup>Université de Mons-Hainaut, Research Center for Molecular Modeling, 20 Place du Parc,  
7000 Mons, Belgium

The macroscopic behaviour of the contact line during the spontaneous spreading of a droplet can be described via hydrodynamical equations (Cox) or in terms of microscopic quantities (molecular kinetic theory), specifically the substrate-liquid and liquid-liquid interactions.

In this talk, we will show how designed molecular dynamics simulations containing a sufficiently large number of atoms can be used to model the spreading of a liquid drop on a solid surface. We will also show that the evolution of the drop may be modeled using the molecular-kinetic theory of wetting.

Furthermore, we will demonstrate that the effective molecular parameters in the theory are consistent with those arising directly from simulation. It will be shown that both simulation and theory reproduce characteristic spreading laws previously arrived at by experiment and based on simple hydrodynamic arguments. More details about the fluxes of the molecules during spreading will also be given.

This presentation will amply demonstrate the power of molecular dynamics simulations in relating the macroscopic dynamics to the microscopic properties of the system.

## 244.B5

### DROPLET SPREADING: MICROSCOPIC APPROACH

T. Blake, A. Clarke, J. De Coninck, M. de Ruijter, and M. Voué

Research Center in Molecular Modelling, Université de Mons-Hainaut  
20, Place du Parc, 7000 - Mons, Belgium

Consider a sessile liquid drop on top of a solid substrate. At the atomic scale, three type of interactions will play a significant role in the phenomenon: the fluid-fluid, solid-solid and fluid-solid interactions. If the fluid-solid interactions are small enough, with respect to the fluid-fluid interactions, it is expected that the drop will remain a drop, transforming itself from some initial configuration into its equilibrium shape, minimizing thus the free energy of the system wall+drop. However, it is also clearly expectable that if the fluid-solid interaction is rather strong, the drop will transform itself into a film to maximize its contact with the solid surface. Eventually, depending on the details of the disjoining pressure, the film will be a monolayer covering the substrate.

Many beautiful experiments have been performed to study the dynamics of these phenomena, not only within partial wetting but also in complete wetting. The situation is however much less obvious concerning the theoretical models. As already pointed out in many publications, different approaches have been developed which are not always compatible.

The aim of this lecture is to review these different approaches for the dynamics of sessile drops and to emphasize the interest of detailed numerical simulations. This technique can not only lead to the validation of one of the proposed models but can also give an interesting tool to get a better understanding of experimental observations.

### **245.B3**      **STUDY ON THE INCREASE OF WHITENESS OF CALCINED KAOLIN BY USING ADDITIVES**

**Cao Mingli, Yuan Jizu, Pan Yahong**

*Dept. of Non-metallic Resources & Environmental Eng., Wuhan University of Technology,  
Wuhan, P.R. China*

To meet some special requirements such as paper filler, ceramic titanium white powder and synthetic 4 Å zeolite, etc., raising the whiteness of calcined kaolin has become more and more important. The calcination experiments were carried out with and without additives to increase the whiteness of calcined kaolin. Results show that the addition of chloride (A) or oxide (B) or oxide (C) can obviously increase the whiteness of calcined kaolin. Meantime, the mechanism of calcination and increase of the whiteness of kaolin was discussed creatively.

### **246.B5**      **NON-UNIFORM STRUCTURE OF SURFACTANT ADSORPTION LAYERS ON SOLIDS: CONTACT ANGLES DATA**

**V.D. Dolzhikova, B.D. Summ**

*Department of Colloid Chemistry, Moscow State University, Moscow, Russia*

Wetting of solid surfaces of different nature (polymers, quartz, paraffin, gold) modified by preliminary adsorption by ionic and nonionic surfactants has been investigated. Advancing ( $\theta_a$ ) and receding ( $\theta_r$ ) contact angles for surfactant solutions on solid surfaces have been measured by sessile drop method. After modification we investigated advancing contact angles ( $\theta_w$ ) of water drop on modified solid.  $\theta_w$  measurements make it possible to determine with high precision the modifying action of diluted solutions of micelle forming surfactants. Isotherms  $\theta_a(c)$  correspond with the surface tension isotherm  $\sigma_{LV}(c)$ .  $\theta_r$  decrease on increasing the concentration and near the CMC  $\theta_r = 0$ . At low concentrations substantial hysteresis of  $\theta_a$  and  $\theta_r$  was observed. In some cases scattering of contact angles  $\theta_w$  measurements is significant. The water drops on modified surface are asymmetrical. Comparison of contact angles isotherms shows non-uniformity of adsorbed surfactant distribution over the surface. Adsorbed layers may be presented by an "island" model. The "islands" formed by surfactant molecules as a result of surface aggregation partially cover the solid. The latter assumption has been verified by direct surfactant adsorption measurements using quartz microbalance technique.

### **247.B5**      **SEARCHING FOR EQUILIBRIUM CONTACT ANGLE AT A SOLID SURFACE**

**Jaroslav Drelich**

*Department of Metallurgical Engineering, University of Utah, WBB 124, Salt Lake City, Utah 84112, USA*

None of the current techniques for contact angle measurement have a specified methodology for the determination of the equilibrium contact angle at a solid surface. In practice two contact angles are

measured at solid surfaces: the advancing contact angle (the largest contact angle for the system which is measured for the advancing liquid front) and the receding contact angle (the smallest contact angle for the system which is measured for the receding liquid front). The difference between the advancing and receding contact angles is called the contact angle hysteresis. The contact angle hysteresis is commonly used to describe the quality of surfaces examined. A great care, however, should be exercised to draw general conclusions from advancing and receding contact angles on the use and validity of thermodynamic relationships, particularly describing the nonideal surfaces. It appears to be important to investigate the correlation between equilibrium, advancing, and receding contact angles for a variety of solid surfaces. In this regard, the contact angle measurements for water on low-energy surfaces of varying smoothness and heterogeneity patterns were carried out by using the captive-bubble technique. A relaxation of advancing and receding contact angles over a period of several hours was observed. The results were found to be in agreement with previous observations of other researchers that a region of the three-phase contact line remains unstable for an extended period after the liquid front is reinforced to move, recede or advance. The advancing contact angle decreased and the receding contact angle increased, in the systems examined, due to the slow equilibration processes (evaporation, condensation, saturation, etc.) occurring in the region of the three-phase contact line. In some systems, where energetic barriers were small (poor heterogeneity and/or roughness), both contact angles, advancing and receding, reached to one value, which is believed to represent the equilibrium contact angle. For systems with an extended degree of surface heterogeneity and/or roughness, the contact angle hysteresis reached to a smaller value but still a difference between "advancing" and "receding" contact angles was observed. Also, for some of the systems examined, the oscillating-type of curve for the contact angle vs. time relationship was observed; no stability could be obtained in the contact angle over the period of several days. This phenomenon appeared at nonideal surfaces according to evaporation, condensation and coalescence processes occurring in the microscopic region of the three-phase contact line.

## 248.B5      EVAPORATION OF SESILE DROPS ON POLYMER SURFACES: ELLIPSOIDAL CAP GEOMETRY

H.Yildirim Erbil<sup>1</sup> and R.Alsan Meric<sup>2</sup>

<sup>1</sup>TUBITAK, Marmara Research Center, Department of Chemistry,  
P.O. Box 21, 41470, Gebze, Kocaeli, Turkey.

<sup>2</sup>Istanbul Technical University, Faculty of Aeronautics and Astronautics, Maslak, Istanbul 80626, Turkey.

The evaporation rate of sessile drops of water resting on polymethymethacrylate polymer has been studied by using the recently published precise data of Rowan, Newton and McHale. When the usual spherical cap model is applied, the rate of evaporation is found to depend on the radius of liquid-solid interface,  $r_b$ , for different sized drops ( $r_b = 0.293 - 0.585$  nm). Also, the decrease of the contact angle,  $Q$ , with time is found to depend on  $r_b$ . Mathematical expressions for an ellipsoidal cap model are derived. When this model is applied, the surface area and volume of the drops showed to be almost completely linear time dependence, especially for the drops having  $r_b = 0.491$  and  $0.585$  mm. A vapor diffusion model depending on the two radii of curvature of an ellipsoidal cap is also developed similar to Rowan et al. and the expression for the rate of evaporation is found to reduce to that of Rowan et al.'s in the limit as the drop shape becomes a spherical cap geometry.

## 249.B5      HYDROPHOBIC AND SUPERHYDROPHOBIC CHEMICALLY MODIFIED POROUS SILICAS

Alexander Y. Fadeev

Moscow State University, Chemistry Department, Laboratory of Organic Catalysis, Vorob.Gory,  
119899, Moscow, Russia

The problem of hydrophobization of porous silica by covalent bonding of organosilicon monolayers is discussed. The ways of increasing of hydrophobicity of surface bonded layer have been considered.

The following organosilicon modifiers were studied as hydrophobizing agents:

- 1) *alkyldimethylchlorosilanes*:  $\text{ClSi}(\text{CH}_3)_2\text{C}_n\text{H}_{2n+1}$ ;  $n = 1, 4, 6, 8, 12, 16$ ;
- 2) *phenylchlorosilanes*:  $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_3\text{Ph}$ ;  $\text{ClSiPh}_2\text{C}_2\text{H}_5$ ;  $\text{Cl}_3\text{SiPh}$ ;
- 3) *alkyl-(N,N-dimethylamino)silanes*:  $(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_2\text{C}_n\text{H}_{2n+1}$ ;  $n = 1, 4, 8, 16$ ;
- 4) *fluoroalkylsilanes*:  $\text{ClSi}(\text{CH}_3)_2(\text{CH}_2)_2\text{CF}_3$ ;  $\text{ClSi}[(\text{CH}_2)_2\text{CF}_3]_3$ ;  $(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_2(\text{CH}_2)_2\text{CF}_3$ ;  
 $(\text{CH}_3)_2\text{NSi}(\text{CH}_3)_2(\text{CH}_2)_3\text{-R}_f$ ;  $\text{R}_f = \text{i-C}_3\text{F}_7$ ;  $\text{n-C}_6\text{F}_{13}$ ;  $\text{tert-C}_6\text{F}_{13}$ .

Ten porous silicas (silica gels, silochromes) with considerably different geometric-structural parameters were used for hydrophobization. The water porosimetry technique was used for the characterization of surface hydrophobicity. Proposed in [1] the method of water porosimetry involves the investigation of the water intrusion into the pores under the external pressure.

The influence of average pore diameter, bonding density of silane, the nature of anchor group and structure of modifier chain on the hydrophobicity of the modified surface were investigated. Four types of water porograms are observed for fully hydrophobized, partially hydrophobized, and nonhydrophobized porous silicas respectively.

The validity of Laplace equation in a wide range of pore diameter (from 4 to 35 nm) is confirmed. Advancing and receding angles of water on modified silica surfaces are estimated from the water porograms. Contact angles obtained from the water intrusion porograms were compared with those obtained from the direct measurements of capillary rise of water in hydrophobized quartz capillaries.

Hydrophobized silicas which showed the spontaneous extrusion of water after the receding of pressure were referred to as *superphobic*. It is shown that such superphobization of surface was observed only for dense bonded layers prepared from long-chained alkyl silanes (bonding density higher than 2.1 groups/nm<sup>2</sup>) as well as from silanes containing bulky branched perfluorinated group (bonding density higher than 1.8 groups/nm<sup>2</sup>).

1. Eroshenko V.A. and Fadeev A. Y. Method of water porosimetry for investigation of hydrophobic porous solids. Ross. Khim. Zh. (Zh. Ros. Khim. O-va im. D.L. Mendeleeva), 1996, v.40, N1, p.92.

## 250.B5 A NEW CONTACT ANGLE MEASUREMENT TECHNIQUE BY ANALYSIS OF CAPILLARY RISE PROFILE AROUND A CYLINDER (ACRPAC)

Yongan Gu and Dongqing Li\*

Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G8

A new experimental technique to determine the contact angles of capillary rise profiles around a conic cylinder is presented in this paper. In the experiment, a carefully coated conic glass cylinder was inserted vertically and slowly into a measuring liquid. Then a precise digital image of the partial capillary rise profile of the liquid around the conic cylinder was acquired and digitized by applying computer image processing and analysis techniques. From the digitized profiles of the liquid-vapour interface and the conic cylinder, the local inclination angle,  $\beta$ , and the local radius,  $R_c$ , of the conic cylinder at the three-phase contact circle were calculated directly. Furthermore, an objective function was constructed, which expresses the discrepancy between the physically observed capillary rise profile and the theoretically predicted curve, i.e., the curve representing a solution of the Laplace equation of capillarity. The contact angle of the capillary rise profile on the conic cylinder was used as an adjustable parameter in optimizing the objective function and determined once the minimum objective function was achieved. The accuracy of the measured contact angles is approximately 0.1°. In addition to local gravity, densities of liquid and vapour phases and the liquid-vapour surface tension, the input requirement is the digital information of the partial capillary rise profile which is provided by implementing a specially designed computer image analysis and digitization program.

This method was tested to measure the contact angles of four n-alkane liquids around cylindrical glass fibres coated with the FC725 material. The measured contact angles are in excellent agreement with those determined by the Wilhelmy plate technique. The present technique was also applied to study the dependence of contact angles on the geometry of the conic cylinder, i.e., on  $\cos\beta/R_c$ . The contact angles of the four n-alkane liquids on conic glass cylinder coated with the FC725 material were measured at different positions along the cylinder. The results were interpreted in terms of the line tension effect. The calculated

line tensions were positive and of the order of  $1 \mu\text{J/m}$ , consistent with the published data for the similar solid-liquid systems using the sessile drop method. Particularly, the contact angle without the line tension effect for a given solid-liquid system can be measured directly by this method. The validity of this contact angle and line tension in the paper was also confirmed by the Axisymmetric Drop Shape Analysis (ADSA) technique. Finally, this new technique is especially suitable to study wetting and spreading phenomena of a liquid on fibres as most natural and artificial fibres are porous and their shapes may vary along the length direction. As an important application, this technique was applied to measure the advancing and receding contact angles of three liquids on six cylindrical polymeric fibre samples which were used as capillary membranes in haemodialysis. A general user-oriented computer program to implement the technique was developed.

## 251.B5 FILM TRAPPING TECHNIQUE: PRECISE METHOD FOR THREE-PHASE CONTACT ANGLE DETERMINATION OF MICROMETER SIZED PARTICLES

A. Hadjiiski<sup>1</sup>, N. D. Denkov<sup>1</sup>, T. D. Gurkov<sup>1</sup>, I. B. Ivanov<sup>1</sup>, and R. Borwankar<sup>2</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, Sofia University, 1126 Sofia, Bulgaria

<sup>2</sup>KRAFT General Foods Inc., Technology Center, 801 Waukegan Road, Glenview, IL 60025, USA

We developed a novel method for determination of the three-phase contact angle at the surface of a micrometer sized particle (latex sphere, oil droplet or biological cell). The latter is entrapped within a liquid film of equilibrium thickness smaller than the particle diameter. Thus a liquid meniscus (a layer of uneven thickness) is formed around the particle. When observed in reflected monochromatic light, this meniscus appears as an interference pattern of concentric bright and dark fringes. From the radii of the interference fringes one can restore the meniscus shape by using the solution of the Laplace equation of capillarity. When applied to solid spheres, the method provides values of the three-phase contact angle particle-water-air. When applied to deformable (fluid) particles, the method allows to determine the thermodynamic quantities characterising the asymmetrical film which appears at the contact of the particle with the surface of the larger film: contact angle film-meniscus, adhesion energy, disjoining pressure, film tension, etc. The contact angles of latex spheres from several batch samples (produced by Interfacial Dynamic Corp., Oregon, USA) were measured to fall in the range between  $32^\circ$  for chloromethyl/sulfate latex and  $61^\circ$  for sulfate latex. Experiments with oil droplets, stabilised with adsorbed protein layer, were performed at different pH and ionic strength, and showed rather high values of the contact angle film-meniscus (between  $30^\circ$  and  $50^\circ$ , depending on the particular system). Notably, the capillary pressure the capillary pressure in these experiments was relatively high - typically between 100 and 500 Pa. Further, the method was applied to human white blood cells (lymphocytes) entrapped within a film stabilised by serum protein and IgG. The contact angle at the periphery of the contact zone of the cell with the protein adsorption layer, as well as the membrane tension of the cell, were determined.

"Film Trapping Technique: Precise Method for Three-phase Contact Angle Determination of Solid and Fluid

Particles of Micrometer Size", A. Hadjiiski et al., *Langmuir* 12 (1996) 6665-6675.

## 252.B5 SURFACE FREE ENERGY COMPONENTS OF BARITE: THE EFFECT OF SODIUM DODECYL SULFATE ADSORPTION

Lucyna Holysz and Emil Chibowski

Department of Physical Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University,  
20031 Lublin, Poland

The approach of van Oss, Good and Chaudhury [1-2] to the formulation of the surface free energy was applied for determination of apolar Lifshitz-van der Waals component,  $\gamma_s^{\text{LW}}$ , and polar acid-base;

electron donor,  $\gamma_s^-$ , and electron acceptor,  $\gamma_s^+$ , components of the tested natural sample of barite (from Poland). The components were determined using two methods: from contact angles and wicking method. The contact angles of practically apolar liquids; diiodomethane and  $\alpha$ -bromonaphthalene, and polar liquids; water, formamide, glycerol, and ethylene glycol, were measured on the compressed pellets of the barite. The wicking method relied on measurements of the penetration rate of apolar and polar liquids into a porous layer of the powdered sample. The surface free energy components were determined from a modified Washburn's equation [3-4]. Using these methods the components were determined both for bare surface, and for the surface with preadsorbed  $\text{DDSO}_4\text{Na}$ . The samples were equilibrated in  $10^{-4}$  and  $10^{-3}$  M solutions of the sulfate, thus giving the adsorbed amounts of 0.465 and 5.44  $\mu\text{mol/g}$ , respectively. It corresponds to 0.5 and 6.0 calculated monolayers. In this later case it means that the adsorption was nonuniform. The determined components of the surface free energy for the bare sample are: 1) from contact angles  $\gamma_s^{\text{LW}} = 48.2 \pm 0.2$  (from diiodomethane),  $\gamma_s^- = 57.8 \pm 9.8$ ,  $\gamma_s^+ = 0.30 \pm 0.36$   $\text{mJ/m}^2$  (average from the liquid pairs: water-formamide, water-glycerol, water-ethylene glycol), 2) from wicking method  $\gamma_s^{\text{LW}} = 48.6 \pm 0.9$  (from n-alkanes and diiodomethane),  $\gamma_s^- = 57.4 \pm 0.1$ ,  $\gamma_s^+ = 0.07 \pm 0.03$   $\text{mJ/m}^2$  (from water-formamide). As it is seen very good agreement of the results is obtained from both methods. However, it should be remarked that although  $\gamma_s^-$  values are practically the same, the standard deviation of the value from contact angle is high ( $\pm 9.8$   $\text{mJ/m}^2$ ). It is because the contact angles were measured on the pellets obtained from the compressed powder of barite. The sodium dodecyl sulfate adsorbed from  $10^{-4}$  M solution alters the  $\gamma_s^{\text{LW}}$  only slightly, from 48.2 to 44.8  $\text{mJ/m}^2$  (contact angle method), or to 46.1  $\text{mJ/m}^2$  (wicking method), and when adsorbed from  $10^{-3}$  M solution, the values are: 43.1 (contact angle) and 51.0  $\text{mJ/m}^2$  (wicking). However, the effect of  $\text{DDSO}_4\text{Na}$  on the electron donor interaction,  $\gamma_s^-$ , is much more pronounced. This component is decreased to  $47.7 \pm 1.5$  ( $10^{-4}$  M) and  $17.2 \pm 2.2$  ( $10^{-3}$  M)  $\text{mJ/m}^2$ . This values were obtained from contact angles (water - formamide and water-glycerol). The wicking method could not be applied because water has not penetrated into the porous layer of such pretreated samples. The electron acceptor component,  $\gamma_s^+$ , has increased a little for both samples pretreated with  $\text{DDSO}_4\text{Na}$ . However, the net result in both cases is the same, the reduced polarity of the barite surface. This can be characterized by the work of spreading of water, which is: 2.8 (bare sample), -3.4 ( $10^{-4}$  M) and -37.8 ( $10^{-3}$  M). Negative value of the work of spreading means that water does not spread over the surface. It reflects in the flotability of barite [5].

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## 253.B5

### STUDIES ON THE SURFACE MODIFICATION OF ANHYDRITE

Chen Jichun, Bi Xiaoping, Peng Changqi

Department of Resources and Environmental Engineering, Wuhan University of Technology,  
Wuhan, China 430070

The lack in the early phase gelation property has limited the application of anhydrite as a building material products. The use of additives, however, activates the anhydrite surfaces and results in the occurrence of early phase gelation. Under different surface modification conditions, the solubility of anhydrite in water have been measured and they have indicated a correlation between the anhydrite surface activity and its solubility in water. This relationship can be utilized to further study the anhydrite surface activation.

## 254.B5 CHARACTERIZATION OF MODIFIED MEMBRANES BY MEANS OF CONTACT ANGLE MEASUREMENTS

H. Kamusewitz<sup>1</sup>, M. Diamantoglou<sup>2</sup>, D. Paul<sup>1</sup>

<sup>1</sup>GKSS Research Centre Geesthacht GmbH, Institute of Chemistry, Kantstrasse 55,  
D-14513 Teltow, Germany

<sup>2</sup>Akzo Nobel Central Research, D-63784 Obernburg, Germany

The characterization of interfaces between membranes and test liquids by means of contact angle measurements makes it possible to evaluate thermodynamic quantities, which can be used to explain interfacial phenomena. All of the theoretical approaches are based on the knowledge of the so-called YOUNG's angle. Its direct observation is only possible if the solid is rigid, homogeneous and smooth. In experiments with real membranes these conditions are only fulfilled approximately, since roughness and local fluctuations of interfacial tensions are present. As a result of this, advancing- and a receding-angles appear and the importance of the roughness and heterogeneity seems to be crucial.

Using different methods, the contact angle hysteresis was measured, firstly on rough and homogeneous membranes, and compared with model-theoretical considerations. The approach developed in this investigation permitted the estimation of the relevant YOUNG's angle. The hysteresis was observed secondly on modified cellulosic membranes with different degree of modification as an example of smooth and heterogeneous separation layers.

## 255.B5 CHARACTERISATION OF POLYMER BEADS FOR BIOMAGNETIC SEPARATION

Emilie Lasson, Siri Stabel Olsen, Vidar Skagestad, Diem Tran, Evy Viken

*Dynal A.S, Oslo, Norway*

Magnetic polymer beads for separation in biochemical and biomedical research is a well established concept. The technique is based on coating of a magnetic polymer particle with specific ligands with affinity to the target. The basic polymer bead has traditionally been hydrophobic, but hydrophilic beads with more specific binding characteristics are now entering the market. Both the chemical and biochemical modification on these particles are dependent on their surface characteristics. This also governs how they will interact with each other, with the surrounding medium and with biomolecules.

Various particles (hydrophobic and hydrophilic) have been characterised, both macroscopically by studying their charge and contact angle and by different spectroscopic techniques in order to characterise their functionality. Various types of optical and electron microscopy are also used to look at their dispersive characteristics and their surface morphology. The results between the different techniques will be compared and evaluated. The biological functionality of the beads will be commented in correlation to their surface characteristics.

## 256.B5 STUDY ON THE SURFACE MODIFICATION OF QUARTZ

Liu Ligen and Tian Jinxing

*Dept. of mineral Resources and envir. Eng., Wuhan Univ. of Tech., Wuhan, P.R. China*

Using silane coupling agents, this paper studied the surface modification of quartz from Panzhihua in Sichuan province and its application in complex filling materials. The results showed that when the filled quantity of the surface modified quartz was 20-50 % (wt), the mechanics properties and the corrosion-resistant properties of the complex filling materials were improved. The deformation temperature of the complex filling materials was raised. The mechanism of the reaction between the silane coupling agents and the inorganic materials was described. The concept of activation extent was advanced.



## 257.B5 INTERDEPENDENT CHANGES OF CHEMICAL COMPOSITION AND PHYSICO-CHEMICAL PROPERTIES OF DISPERSE MINERALS IN THE PROCESS OF ACID ACTIVATION

Martsin I.I.

*Biocolloid Chemistry Institute of the NAS of Ukraine*

The process of acid activation of disperse minerals and assumed interdependency of their chemical composition and physico-chemical properties, including the adsorptive and catalytical ones, have been paid a lot of attention. It was stated in many works that to find such an interdependency seemed not to be possible. Therefore, the main content of the majority of works was narrowed to the presentation of disperse minerals chemical compositions before and after the activation. And there were no correlation found except the obvious decrease of content of aluminium, ferrum, magnesium and other cations and increase of content of silica in the acid-activated specimen.

Starting from the knowledge of crystallo-chemical structure of disperse minerals and from the knowledge of certain ratio of cations in each crystal type, the author had determined the level of decomposition (C %) of minerals under effect of acid of different concentrations. Here all levels of decomposition, from 0 for the initial mineral to 100% for the total decomposition, allowed to determine dependencies of physicochemical properties change on C %. It had been found that the changes of surface acidity, specific surface and average pores radius are of different directedness. This accounts for the absence of correlation between adsorbent or catalyst activity and the values of specific surface and acidity. However, each of the examined by the author minerals reveals the decomposition levels which yield the same directedness of activity and physicochemical properties.

The established dependencies allow to perform aimfully the acid activation of disperse minerals with subsequent production of highly active adsorbents and catalysts.

## 258.B5 MODIFICATION OF TEFLON SURFACE BY SYNTHETIC POLYELECTROLYTES AND BY THEIR ASSOCIATES WITH SURFACTANTS

Omarova K.I., Musabekov K.B.

*Kazakh State National University, Department of Chemistry, Almaty, Vinogradov str., 95, Kazakstan*

A most appropriate method of varying solid surface properties is the adsorption of surfactants from aqueous solution. This method excludes the use of fire-hazardous or toxic organic solvents. Besides the directional orientation of surfactant molecules in the adsorption layer strongly bound with the solid surface. Irreversibly - adsorbable water-soluble polymers, the adsorption layer thickness of which reaches rather high values (70-100Å), seem to be most perspective in this respect.

This work is aimed as studying influence of nature, concentration, molecular weight of polyelectrolytes and surfactant additions on the adsorption, wetting and electrokinetic potential of teflon. For this purpose, such polybases as hydrochloride poly-2-methyl-5-vinylpyridine (PMVP), polyethylene imine (PEI), and polyacrylic (PAA) and polymethacrylic (PMAA) acids and SAS-dodecylsulfate sodium (DDS) and cetylthreemethyl ammonium bromide (CTAB).

The extremal water-wetting isotherms of teflon relationship evidences different adsorptions from diluted ( $<10^{-3}$  %) and from concentrated solutions. The structure of adsorption layers depends of the conformation, the molecular weight, hydrophobic of SPE macromolecules and solid surface treatment. The adsorption of synthetic polyelectrolytes (PMVP and PEI) over fluoroplast- 3M powder, determined by spectrophotometry, increases with growth of concentration. The sign of  $\zeta$ -potential of teflon coincides with that of the macroion adsorbed. With growth of the molecular weight, hydrophobic nature macromolecules increases the hydrophilization effect of polyelectrolytes on teflon surface, which is higher for cationic polyelectrolytes (PMVP, PEI).

The simplest way of changing the hydrophobic nature of polymer chains is to introduce a surfactant into the polyelectrolyte solution with a charge opposite to that of macromolecules. The components of mixture interact by the ion-exchange mechanism and from polyelectrolyte associates of surfactants. The adsorption of associates on teflon surface leads to decrease of the wetting angle which is particularly

appreciable in the region of maximum electrostatic binding of surfactants by polyelectrolytes. The mixtures of polyelectrolytes and SAS exert a stronger hydrophilization effect on teflon surface compared with separate polyelectrolytes and SAS.

The electrokinetic potential of teflon, measured in aqueous solutions of SPE and surfactant mixtures, conform the assumption of the polyelectrolyte associates adsorption on teflon surface. Zero values of teflon  $\zeta$ -potential correspond to zero values of  $\zeta$ -potential of associates and to relative concentrations of surfactants with the highest strength of electrostatic binding of SAS with polyelectrolytes.

## 259.B5 INFLUENCE OF DOUBLE ELECTRIC LAYER OF THE ACID-BASE REACTIONS IN SOLID-LIQUID INTERPHASES

A.B. Pecheny, V.L. Budarin, V.N. Zaitsev

*T.Shevchenko Kiev University, Chemistry department, 60 Vladimirska Str., Kiev 252033 Ukraine*

Double-electric layer developing on the silica surface as the result of protonation or dissociation of its functional groups has essential influence on the acid-base equilibrium in solid-liquid interfaces. Analytical expressions describing interrelation between the electrostatic phenomena and acid-base properties of functional groups on the surface of solid materials are not till now received. In the present work the attempt to discuss this question is made. On the basis of the assumptions that: 1) surface potential is only the result of chemical reaction; 2) equilibrium constant that describes the reaction in the interface ( $K_s$ ) has relation with the appropriate constant in solution ( $K_L$ ), such as  $K_L = \chi K_s$ ; 3) the double electric layer is described by Gou-Chapman theory; the equations for surface potential ( $\psi$ ) in electrolyte absence were obtained:

$$\psi = \frac{RT}{zF} \ln \left( 1 + \left( (1 - \alpha_s) \alpha_s K_L \chi^{-1} B C_L^2 \right)^{1/2} \right),$$

where  $B^{1/2} = \frac{zF}{(2\epsilon\epsilon_0 RT)^{1/2}}$  and  $\epsilon$ -dielectric constant of the solvent;  $\epsilon_0$ -dielectric in vacuum,  $R$ -universal gas constant,  $z$  anion charge,  $F$ -Faraday number,  $C_L$  - concentration surface functional groups,  $\alpha_s$ -completeness of the reaction.

If strong electronic with concentration  $C$  is present, then :

$$\psi = \frac{RT}{zF} \ln \left( 1 + \frac{B C_L^2 C^{-1} \alpha_s}{2} + \frac{B^{1/2} C_L C^{-1/2} \alpha_s^{1/2} (4 + B C_L^2 C^{-1} \alpha_s)^{1/2}}{2} \right).$$

Analysis of the equations obtained has shown, that surface potential developing during reaction results in shift of titration curve for immobilised basic organic groups towards acid pH, but for acidic surface groups the shift is in reverse order towards basic region. The equations describing titration curves for covalently bonded functional groups with respect to surface potential was also obtained. It was shown that with increasing of electrolyte concentration surface potential is decreased. It reflects in reduction of shift value for titration curve and found good experimental proof.

## 260.B5 SURFACE CHARACTERISATION OF KEVLAR® FIBERS BY INVERSE GAS CHROMATOGRAPHY

S. Rebouillat<sup>1\*</sup>, and J.B. Donnet<sup>2</sup>

<sup>1</sup>*Du Pont (UK) Limited, Maydown Research Centre, PO Box 15, Londonderry BT47 1TU, UK*

<sup>2</sup>*Laboratoire de Chimie Physique, Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue, Alfred Werner, 68093 Mulhouse Cedex, France*

Surface energy properties of three poly (p-phenylene terephthalamide) fibers (Kevlar®) have been studied by inverse gas chromatography (IGC), at both infinite dilution and finite concentration. The results show the usefulness of these techniques.

At infinite dilution, the IGC is a suitable method to determine the dispersive component of the surface free energy and the specific term due to acid - base interactions or electron acceptor - donor characteristics. It is even possible to attribute an acidic constant  $K_A$  and a basic constant  $K_B$  to the fibre surface which may allow a useful comparison with the polymer used as matrix.

Inverse gas chromatography at finite dilution is a good technique for the determination of the sorption properties of the fiber. It gives access to the adsorption isotherms of various gaseous probes and to the enthalpy of adsorption of the probe molecules. The information obtained leads to a different type of knowledge in comparison to the ultimate surface characteristics obtained at infinite dilution and is complementary to these ones. The enthalpy of adsorption can be compared with the liquefaction energy of the gaseous probe molecule and the specific interactions can be estimated when these two values differ. Unique energy distribution mapping can be derived from the data which for Kevlar® fibers reveals unprecedented characteristics.

Widely used as a reinforcing material in polymer and elastomer composites, the Kevlar® advanced fibers can be uniquely characterised by these IGC techniques.

*Kevlar®: DuPont registered trademark for its high strength para-aramid fibers.*

## 261.B5

### CONTACT ANGLE ON FRACTAL SURFACES

Hideki Sakai, Liu Hui, Tomiko Fujii

*Faculty of Human Life Science, Osaka City University, Osaka, Japan*

In this paper, the equilibrium contact angle on the surface having a fractal dimension  $D$  between 2 and 3 is studied systematically.

It is said that wettability of solid surfaces is determined by the chemical modifications and by the geometrical structure (roughness) of the surfaces. The chemical modifications, e.g., fluorination, addition of surfactant to the liquid, have been used to control the wetting behavior.

On the other hand, the geometrical aspect was not so widely used for lack of its general understanding. However, after the introduction of fractal concept to the wettability of surfaces by Hazlett [1], geometrical aspect is applied to control the wettability of the surface [2]. Here, we concentrate our attention on the geometrical aspect of wettability of solid surfaces.

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## 262.B5

### ANALYSIS OF AXISYMMETRIC MENISCI ABOUT PARTIALLY SUBMERGED RODS

Matthew Schneemilch, Rob Hayes, Stan Miklavcic and John Ralston

*Ian Wark Research Institute, University of South Australia, The Levels, SA 5095, Australia*

The contact angle formed when a solid of cylindrical geometry penetrates the interface between two immiscible phases is obtained by fitting the profile of the meniscus to Laplacian curves, in a fashion similar to that employed in axisymmetric drop shape analysis<sup>1</sup>. Gravity plays a more significant role in determining the solution to the Laplace equation than in the case of small drops. Static and dynamic menisci in rise and depression are imaged with a CCD camera and high resolution optics. The images are digitised and edge detection is employed to locate the interface. The algorithm used to solve the Laplace equation was developed by Huh and Scriven<sup>2</sup> and has been incorporated in an automated fitting package which takes the raw image, performs various methods of edge detection, and determines the region which is undistorted through least squares curve fitting. Hydrodynamic distortion of dynamic menisci<sup>3</sup> is experimentally detectable with this apparatus and distinguishable from distortion which is purely optical in nature. The effect of acceleration on the dynamic contact angle is also investigated as is the apparent stick-slip motion of the contact line. Direct image capture to video recorder facilitates the investigation of the dynamic meniscus over small time intervals. Averaged values of the contact angle at various contact line speeds are used to test

the current theories of dynamic wetting. The improved optics and greater accuracy in contact angle determination via this technique provide new insights into the wetting process.

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## 263.B5

### LANGMUIR-BLODGETT TECHNIQUE IN WETTING STUDIES

S. Semal, T. Blake, M. Voue, J. De Coninck

*Université de Mons-Hainaut, Centre de Recherche en Modélisation Moléculaire,  
20, Place du Parc, 7000 Mons, Belgium*

The LB technique is a surface treatment which consists of depositing a liquid film on a solid substrate. The modified properties are for example wettability, surface energies, roughness...

A large variety of solids and liquids can be used as substrates (glass and silicone wafer ...) and as covering liquids (fatty acids ...).

To control the quality of the LB-films we use three means of characterization: AFM, dynamic contact angle (DCA) measurements and ellipsometry.

AFM allows to control the quality of LB-films and to measure their roughness.

DCA measurements show that hysteresis of contact angles decreases when the number of layers increases. Minimum hysteresis is reached for a given number of layers and this number decreases when the length of fatty acid molecules increases. Extrapolation of the advancing angle curve versus speed for speed reaching zero allows to obtain the static contact angle. Fitting this curve with the molecular kinetic theory by T. Blake allows to determine parameters which are characteristic of the surface relating then the number of layers and roughness.

Ellipsometry allows to control the thickness of LB-films.

The poster will be devoted to the presentation of the dynamic contact angle measurements versus the number of considered layers. Relationship with the molecular kinetic theory will be emphasized.

## 264.B5

### SUPER WATER-REPELLENT SURFACES RESULTING FROM FRACTAL STRUCTURE

Satoshi Shibuichi<sup>1</sup>, Tomohiro Onda<sup>2</sup>, Naoki Satoh<sup>1</sup> and Kaoru Tsujii<sup>1</sup>

<sup>1</sup>Tokyo Research Center, Kao Corporation, 2-1-3 Bunka, Sumida-ku, Tokyo 131, Japan

<sup>2</sup>Recording and Imaging Science Laboratories, Kao Corporation, 2606, Akabane, Ichikai-machi, Haga-gun, Tochigi, 321-34, Japan

Wettability of solid surfaces with a liquid (water in particular) is quite important phenomenon in our daily life as well as in many industrial processes. The wettability is governed by the two factors. One is the chemical factor, and the other is the geometrical (surface structural) factor of the solid surfaces. Water-repellent surfaces are usually designed by the former factor utilizing the low surface free energy of fluorinated compounds. We have paid special attention to the geometrical structure of solid surfaces, and found the excellent effectiveness of fractal structure on the wettability<sup>1</sup>. The present paper deals with the theoretical treatment on the wettability of fractal surfaces and the experimental realization of the super water-repellent surfaces which repel completely the water droplet.

A theory on the wettability of fractal surfaces has been established<sup>1</sup>. The relationship between the contact angle of the flat surface  $\theta$  and that of the fractal surface  $\theta_f$  is expressed by the equation;  $\cos\theta_f = (L/l)^{D-2} \cos\theta$ , where  $(L/l)^{D-2}$  is the surface area magnification factor, and  $D$  is the fractal dimension,  $L$  and  $l$  the largest and the smallest size limits respectively between which the self-similar (fractal) structure holds. One can see from the above theoretical prediction that the fractal surface can be a super liquid-repellent or a super-wettable one, since the surface area magnification factor can be much greater than unity.

Super water-repellent surfaces showing the contact angle of  $174^\circ$  for water droplet have been actually made of alkylketene dimer (AKD). Water droplets roll around without attachment on the super water-repellent surfaces when tilted slightly. The AKD is a kind of wax, and forms spontaneously a fractal structure in its surfaces. Super water-repellent surfaces were prepared by solidification from the melted AKD. The melted AKD was cooled down to room temperature in the dry nitrogen gas atmosphere, and was allowed to solidify. The water-repellency of the AKD surface progressively improves for about 3 days, and finally shows the super water-repellency having the contact angle larger than  $170^\circ$  without any fluorination treatments. Figure 1 shows a photograph of a water droplet of  $\sim 1$  mm diameter on the superwater-repellent AKD surface. The fractal dimension  $D$  of the solid AKD surface was determined to be  $D \sim 2.3$  applying the box counting method to the SEM images of the AKD cross section.  $L$  and  $l_e$  also estimated from the box counting method. The contact angles of some water/1,4-dioxane mixtures on the fractal and the flat AKD surfaces were determined, and the values of  $\cos\theta_f$  were plotted against  $\cos\theta$ . The plot of  $\cos\theta_f$  against  $\cos\theta$  agrees well with the theoretical prediction. It has been demonstrated by this work that the fractal concept is a powerful tool to develop some novel functional materials.



Figure 1

I. Onda, T., Shibuichi, S., Satoh, N., Tsujii, K., *Langmuir*, 12,2125 (1996).

## 265.B5

### WETTABILITY OF NEW ORGANOSILICON AND FLUOROORGANOSILICON MONOLAYERS, BONDED ON QUARTZ

Soboleva O., Fadeev A.

*Moscow State University, Chemistry Department, Moscow, Russia*

Chemically bonded monolayers of organosilicon and fluoroorganosilicon compounds on quartz were prepared. Chemical modification of previously hydroxylated quartz capillaries was performed under anhydrous conditions using corresponding silanes as follows:  $\text{RSi}(\text{CH}_3)_2\text{X} + \text{HO}[\text{SiO}_2] \rightarrow \text{RSi}(\text{CH}_3)_2\text{O}[\text{SiO}_2] + \text{HX}$ ;  $\text{X} = (\text{CH}_3)_2\text{N}-$ ,  $\text{O} \begin{smallmatrix} \diagup \diagdown \end{smallmatrix} \text{N}-$ ;  $\text{R} = \text{C}_n\text{H}_{2n+1}$  ( $n=1, 4, 8, 16$ );  $(\text{CH}_2)_2\text{CF}_3$ ;  $(\text{CH}_2)_3\text{-n-C}_3\text{F}_7$ ;  $(\text{CH}_2)_3\text{-i-C}_3\text{F}_7$ ;  $(\text{CH}_2)_3\text{-n-C}_6\text{F}_{13}$ ;  $(\text{CH}_2)_3\text{-tert-C}_6\text{F}_{13}$ . Among known alkyl-N,N-dimethylaminosilanes, new alkyl- and fluoroalkyl-N-silylmorpholines were used as modifiers of quartz. Wetting of bonded monolayers by water, hydrocarbons (octane, dodecane and pentadecane) and ethylene glycol under advancing and receding conditions had been studied. The method of capillary rise was used. Zisman critical surface tension  $\sigma_c$  for chemically bonded monolayers were determined. For hydrocarbon monolayers  $\sigma_c$  coincide with critical surface tension of paraffin oil (23 mN/m), for fluorocarbon monolayers  $\sigma_c$  values were smaller (the minimal value of  $\sigma_c = 14$  mN/m for  $(\text{CH}_2)_3\text{-n-C}_3\text{F}_7$  and  $(\text{CH}_2)_3\text{-n-C}_6\text{F}_{13}$ ). Significant wetting hysteresis for water was observed (the maximal gap  $\theta_a - \theta_r = 26^\circ$ ). The hysteresis has place because of approximately 25% of surface silanol groups remains unreacted. For hydrocarbons the hysteresis was not observed. It was demonstrated, that additional treatment of the samples with large excess of trimethylsilane didn't influence on the wettability of monolayers by water. Correlations between wettability and structure of bonded groups (chain length, chain branches, presence of perfluorinated moieties, etc.) were established. It was demonstrated, that only deep fluorination of chain leads to surface with considerably lower surface energy than hydrocarbons. In homologous series -  $\text{C}_n\text{F}_{2n+1}$  contact angles grow with  $n$ . Branching of the modifier molecules results in the increase of  $\theta_a$  and  $\theta_r$  of water.

**266.B5****CHARACTERIZATION OF SOLID SURFACES  
BY MEANS OF MICRO CONTACT ANGLES****K.W. Stöckelhuber, H.J. Schulze***Max-Planck-Institute for Colloids and Interfaces,**Research Group at the Freiberg University of Mining and Technology, Freiberg/Saxony, Germany*

Measuring of contact angles is one of the most important tools to characterize wetting properties of solid surfaces. The measured contact angle, determined by drops with a typical diameter of some millimetres, however shows only an integral value of the surface, not considering i.e. small hydrophobic spots causing the rupture of wetting films. Our aim is to investigate solid surfaces with small droplets to get more information about wetting processes on a more microscopic length scale. These droplets are produced by condensing the moisture of air on the sample, cooled by a peltier thermostat. These drops with a diameter of 10 to 100 micrometers are observed in monochromatic light by a reflecting microscope. On a hydrophilic substrate, height information of the droplets can be determined directly by analysing the observed Newton fringes. So an estimation of contact angles in micrometer scale gets possible.



fig. 1: micro droplets on hydrophilic glass

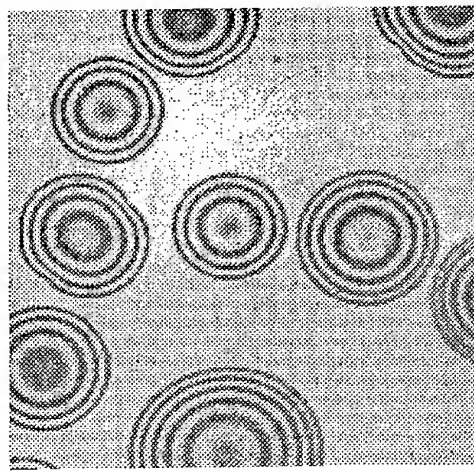


fig. 2: micro droplets on freshly cleaved mica

Freshly cleaned glass with an homogeneous macroscopic contact angle of  $10^\circ$  shows on micrometer scale contact angles between  $4^\circ$  and  $20^\circ$  (fig. 1); whereby the irregular shape of the droplets is a sign for the heterogeneity of the surface.

On freshly cleaved mica (fig. 2) in comparison, the droplets have a axisymmetrical shape and consequently homogeneous contact angles. Here the values scatter only between  $4^\circ$  and  $5^\circ$ .

In the case of micrometer droplets, line tension terms have - as a consequence of the modified Young-Neumann equation - a not negligible influence on the measured contact angles. By measuring the dependence of the droplet size on the contact angle it is possible to estimate a line tension value on these very hydrophilic substrates. We determined a line tension value on freshly cleaved mica of magnitude of  $10 \cdot 10^{-9}$  Newton.

**267.B5****POTENTIAL-INDUCED CAPILLARY EFFECTS ON POLYMER  
FILM-COATED ELECTRIFIED INTERFACES****W.J.J. Welters and L.G.J. Fokkink***Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands*

The formation of electrical double layers on hydrophobed electrode surfaces may lead to pronounced potential-dependent changes in the wettability. These phenomena have been pioneered on gold electrodes, modified with a self-assembled thiol layer (e.g. Sondag-Huethorst and Fokkink, J. Electroanal.

Chem. 367, 49, 1994). Much larger and reversible electrowetting effects have been obtained on (optically transparent) conductors covered with a vapour phase deposited polymer (parylene) film, several microns in thickness, surface finished with a thin teflon-like toplayer. In this paper, contact angle effects (as large as  $110^\circ \rightarrow 60^\circ$ ) between an electrolyte droplet and the parylene-modified surface as a function of potential (up to several hundreds of Volts) and coating thickness will be presented and discussed within the theoretical framework developed. In combination with Laplace capillarity, the electrowetting effect allows for fast and reversible, electrically switchable, capillary rise and fall in surface-modified capillary lumen. Several potential applications of this electrowetting phenomenon, ranging from shape-controllable optical lenses to dynamic filter structures, will be briefly touched upon.

## **268.B5 STUDY ON THE SURFACE TREATMENT MECHANISM OF WEATHER-RESISTANT PEARLESENT PIGMENTS**

**Zhang Gaoke Zhu Yingbo**

*Non-metallic Mineral Design and Research Institute, Wuhan University of Technology, Wuhan, P. R. China*

The methods of synthesis and surface treatment and the treatment agents were described in this paper. The formation of coating film of the weather-resistant pearlescent pigments was studied. The surface treatment mechanism of weather-resistant pearlescent pigment was studied by analysing the properties and structure of weather-resistant coating film and mica pearlescent pigments. The SEM and X-ray diffraction analysis were used.

## **269.B5 STUDY ON COATING MECHANISM OF TITANIA-MICA PEARLY PIGMENTS**

**Zhu Yingbo Zhang Gaoke**

*Non-metallic Mineral Design and Research Institute, Wuhan University of Technology, Wuhan, P. R. China*

The coating mechanism of titania-mica pearly pigments was studied by analysing the surface properties of mica flakes and  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  colloid particle and the hydrolysis reaction mechanism of  $\text{TiCl}_4$  solution. The SEM and other analysis methods were used. The optimum coating reaction conditions were found.

## **270.B6 PHASES CONFIGURATION IN THREE-PHASE FLUID SYSTEMS AND HETEROGENEOUS CONDENSATION: A NEGATIVE LINE TENSION INTERPRETATION**

**A.D. Alexandrov<sup>1</sup> and B.V. Toshev<sup>2</sup>**

<sup>1</sup>*Department of Chemistry, South-Western University, 2700 Blagoevgrad, Bulgaria*

<sup>2</sup>*Department of Physical Chemistry, Faculty of Chemistry, Sofia University, 1126 Sofia, Bulgaria*

The Reverse Wilson Chamber (RWC) method has been applied to critical supersaturation measurements in the case of condensation from supersaturated water vapours on the surface of organic liquids; the initial substrate temperature being kept to 298K.

The critical supersaturation found are in flagrant disagreement with those predicted by the classical (Gibbs-Volmer) theory of heterogeneous nucleation. The discrepancy between the theory and experiment would be explained in the framework of the theory of barrierless heterogeneous condensation, which takes into account the negative line tension of the contact-line perimeter.

On the basis of the theory of the barrierless phase-formation we were able to obtain the dependence of line tension upon the macroscopic geometry of the three-phase system; the latter being

expressed in terms of the dimensionless quantity,  $Q$ , defined as a ratio between the works of adhesion and cohesion, respectively.

Our results are in good agreement with the theory of barrierless heterogeneous condensation allowing us to obtain line tension values, which are in reasonable agreement with the theoretical estimations.

## 271.B6 THE ROLE OF INTERPARTICLE FORCES IN NUCLEATION, CRYSTAL GROWTH AND CHIRAL COMPOUNDS SEPARATIONS

Gregory D. Botsaris and Ru-Ying Qian

*Department of Chemical Engineering, Tufts University, Medford, MA 02155, USA*

The classical homogeneous nucleation models have correctly ignored the role of attractive forces between the embryos in a supersaturated solution, in the primary nucleation process. Treating the supersaturated solution as a colloidal dispersion, this paper shows that interparticle forces cannot be neglected in the case of nucleation in the presence of crystals or seeds in the solution (secondary nucleation). In that case the long range forces between the large crystal and the embryos are important. They lead to a high concentration of embryos near the crystal surface, which in turn leads to high coagulation rates and to the formation of particles whose size exceeds the critical nucleus size. These nuclei forming next to the crystal face may a) be the source of secondary nuclei, if they are removed into the supersaturated solution, and b) affect the growth process of the crystal, by attaching themselves on the surface and being thus incorporated into the growing crystal. The role of these phenomena on the separation of chiral compounds by preferential crystallization (seeding) will be particularly discussed. They will affect the chirality of the formed crystals as well as their purity.

## 272.B6 A STUDY ON MECHANISM OF LIESEGANG'S PHENOMENA

Hideo Funakoshi<sup>1</sup>, Ryohei Matuura<sup>2</sup>

<sup>1</sup>*Fukuoka University of Education, 729, Akama, Munakata-shi, -Fukuoka-ken, 811-41, Japan.*

<sup>2</sup>*Department of Chemistry, Kyushu University, 6-10-1, Hakozaki, Higashi-ku, Fukuoka-shi, 812-81, Japan.*

In the 5th ICSCS (in 1985), the authors reported on the following experimental results of DSC for lithium soaps.

(1) Apparently, three (or more) phase transitions are used to be observed in the cooling run from melt to a room temperature of DSC, and the behaviors of their phase transitions are not always same, depending on the condition of measurement, such as cooling speed.

(2) However, it is concluded that in reality the apparent phase transitions which are due to stepwise crystallizations in the cooling run, resemble that of Liesegang's phenomena, and the complicated behaviors of the stepwise crystallizations can be always put in an experimental expression,

$$(T_o - T_n) = (T_o - T^*) \exp[-(\Sigma \Delta S^* - \Sigma \Delta S_{n-1})/mR],$$

where  $\Sigma \Delta S^*$  and  $\Sigma \Delta S_{n-1}$  are total molar entropy change due to all crystallizing transitions and due to the transitions appeared before the  $n$ th crystallizing transition in the cooling run of DSC.  $T_o$ ,  $T_n$ , and  $T^*$  are the end point of fusion, the  $n$ th crystallizing transition point and an imaginary end point of crystallization at  $(\Sigma \Delta S^* - \Sigma \Delta S_{n-1}) = 0$ .  $R$  is gas constant.  $m$  and  $T^*$  are obtained graphically from the plot of  $(\Sigma \Delta S^* - \Sigma \Delta S_{n-1})$  vs.  $\ln(T_o - T_n)$ .

(3) The experimental equation described above is essentially coincident with an expression given to a fluctuation of crystallization and it is confirmed that the equation can be applied to not only the stepwise crystallizations of lithium soaps, but also to that of cholesteryl laurate reported by Barrall II et al.

Although  $m = 1$  is obtained for cholesteryl laurate,  $m = 2$  for lithium palmitate.  $m$  might be related to assembly of molecule as kinetic unit during crystallizing process.

Since then, the authors have been looking for the method for investigating the mechanism of Liesegang's phenomena using the idea described above. Lately, it has been found that it is possible to estimate the concentrations of components of Liesegang's layer in gel, using a X-ray micro analyser, although it is difficult fundamentally to apply the method to gel system containing much amount of water.



In this conference, it will be reported that behaviors of Liesegang's phenomena in gel (for example, magnesium hydroxide) also are representable perfectly in the same viewpoint.

## 273.B6 FLUCTUATIONS OF CONCENTRATIONS OF NEW PHASE EMBRYOS IN NUCLEATION THEORY

A.P. Grinin, A.V. Karatchentsev

*Department of Statistical Physics, St. Petersburg State University, St. Petersburg, Russia*

An occasional event of new phase embryo formation and, correspondingly, the occasional character of values for the concentration of embryos of a given size mean that all the characteristics of phase transition in the metastable system are occasional at the same extent. The development of the theory which would be able to predict the probabilities for values of the phase transition characteristics is certainly important. The first step in this direction is derivation of the kinetic equation for probabilities of values of new phase embryo concentration. The step is presented in this report. It is remarkable that this derivation turns to be possible in frames of basic positions of the classical theory of nucleation. The fact that the Poisson distribution appears to be the equilibrium and the steady solution of the kinetic equation agrees with the fundamental principles of statistical mechanics. The study of the relaxation properties of the equation shows the existence (under conditions of validity of the macroscopic description of the nucleation process) of the time scale hierarchy which is needed for solving non-linear problems associated with real phase transitions allowing for changing the background conditions of new embryos formation as a result of consumption of the metastable phase matter by the existing embryos.

## 274.B6 BUBBLE NUCLEATION FROM GAS CAVITIES

S. Jones, G. Rigby, K.P. Galvin, and G.M. Evans

*Department of Chemical Engineering, The University of Newcastle, NSW 2308 Australia*

The production of bubbles from a gas cavity in a solution of carbon dioxide and water was observed using a CCD camera and microscope objective. A bubble suddenly "appeared" on the video screen, with the bubble diameter,  $D$ , increasing with the time,  $t$ , according to the law of Scriven (1959),  $D^2 = At$ , with  $A$  as a constant. At a diameter,  $D_{\max}$ , the bubble detached from the substrate, presumably because the net weight force of the bubble exceeded the force of adhesion between the bubble and the substrate. After a relatively significant period of time, a new bubble suddenly appeared at the same location, and repeated almost exactly the growth of its predecessor. In some experiments, this cycle was repeated for hours, until eventually the site produced its last bubble. Interestingly, the final bubble grew at a finite rate indicating that the solution was still supersaturated.

Although the growth of the bubbles are well understood, and the physics governing the condition for the detachment of the bubble is well appreciated, the time required for bubble nucleation is poorly understood. The focus of this study was on the physical factors governing the "nucleation time".

The experimental work was conducted in glass vessels, cleaned using a combination of an alkali treatment over more than 24 hours, rinsing with ultra pure water, chromic acid, and further rinsing with water. In some cases the glass substrate was made hydrophobic using a treatment of trimethylchlorosilane. The ultra pure water used in the test work was dispensed from a Milli Q system. The test solution was prepared *in-situ* by sparging ultra pure water with high purity carbon dioxide. The system was jacketed for temperature control, and saturated at 1°C, and atmospheric pressure. Supersaturation, at the same pressure, was achieved gradually by heating the jacket to a temperature sufficient to produce bubbles from the vessel wall. In some experiments, the bubbles were produced from sub-microscopic sites in the glass, and in other experiments using a well defined cavity in the form of a capillary tube.

The level of supersaturation was always far too low for classical nucleation theory to apply. Therefore, a theory based on the rate of mass transfer was considered. Excellent agreement between the mass transfer theory, and experimental analyses of the cycles of bubble production at the submicroscopic sites, and at the much larger capillary sites was obtained. The work showed that the cycle was governed by

the simple law,  $1/t_g = 1/t_g^* + N/t_n$ , where  $t_g$  is the bubble growth time,  $t_g^*$  is the growth time of the last possible bubble,  $t_n$  is the bubble nucleation time, and  $N$  is a constant. The nucleation times were comparable, or even much longer, than the corresponding growth times. This result seemed remarkable given that in one case the final bubble volume was probably more than 100,000 times greater than the cavity volume. It was concluded that much of the zone around the bubble, depleted of carbondioxide, remained above the cavity following the bubble detachment. So, a mass transfer period comparable to the bubble growth time, was needed to restore the supersaturation level adjacent to the cavity. Consequently, the nucleation times were much longer than expected. Further analysis using computational fluid dynamics is continuing in order to verify the conclusion, and predict the value of  $N$ .

## 275.B6

### THE CALCIFICATION OF FIBRIN IN VITRO

S. Koutsopoulos, E. Koulouri, E. Panouklia, K. Karavoltso and E. Dalas

*Dept. of Chemistry, University of Patras, Greece*

In the present work we employed fibrin in order to assess its capability inducing biological mineralization

Fibrin is a very important factor in the blood-clotting system. Structurally fibrin is an ordered organic matrix which has a periodic structure that repeats every 230 Å.

Hydroxyapatite, HAP and Octacalcium phosphate, OCR are the most interesting calcium phosphate salts. HAP is thermodynamically the most stable calcium phosphate which is mostly used as a model compound for the study of biological calcification processes. On the other hand OCR has been proposed as a precursor of hydroxyapatite whose formation is favoured kinetically in solutions supersaturated to both salts.

The kinetics of crystallization of HAP and OCR on fibrin were studied using the constant composition technique. The onset of HAP crystallization started immediately after inducing the substrate in the supersaturated solution. Unlike HAP crystallization induction periods were observed before the appearance of OCR precipitate in solutions supersaturated with respect to both HAP and OCR.

Using nucleation rate equations derived from classical homogeneous nucleation theory, interfacial energies and the size of the critical nucleus for both HAP and OCR were calculated.

Phosphate was taken up extensively by the biological molecule studied. The dependence of adsorption upon ionic strength and pH of the medium suggests an appreciable contribution of electrostatic forces. Controversially calcium ions did not exhibit any detectable adsorption from solutions containing calcium dichloride at concentrations ranging from  $1 \cdot 10^{-4}$  to  $5 \cdot 10^{-3}$  M in 0.15 M NaCl supporting electrolyte, 37 °C, pH=7.4.

From the results above it follows that formation of HAP on fibrin may be initiated via adsorption of inorganic phosphate on the biological substrate.

## 276.B6 HETEROGENEOUS NUCLEATION OF N-ALCOHOLS FROM SOLUTION ASSISTED BY VAPOR-DEPOSITED AMPHIPHILIC FILMS

S. Nagahisa, H. Takiguchi, K. Iida, S. Ueno, J. Yano, K. Sato

*Faculty of Applied Biological Science, Hiroshima University, Higashi-Hiroshima, 739, Japan*

*In-situ* observation has been done on the acceleration phenomena of nucleation of long-chain n-alcohol crystals, here with referred to guest solutes, assisted by vapor-deposited thin film of amphiphilic molecules, referred to templates. Two types of templates were examined: long-chain fatty acids having even-numbered carbon atoms of 16 through 22 and monostearin. The even-numbered carbon atoms of the guest n-alcohol solutes examined here ranged from 16 to 20. The vapor-deposition of the template films was performed on glass plates in an ambient vacuum. The molecular orientation of the long-chain template films, either normal or parallel to the glassplate, was regulated by choosing the temperatures of the glass substrate and the evaporating furnace placed in the vapor deposition system. The crystal structures of the template film were analysed with X-ray diffraction, atomic force microscopy and FT-IR spectroscopy (1).

The nucleation processes were observed by an optical microscope, on the stage of which the temperature-controlled growth cell filled was placed. The template films was set on the top of the growth cell in contact with the solution, and thereby the nucleation of the guest crystals assisted by the template was monitored unambiguously without confusion with spontaneous nucleation occurring in a free solution space. In the all experiments, the supersaturation with respect to the guest solute was reduced so that the nucleation without the template film did not occur over several hours. It was confirmed that the template and guest molecules were immiscible in bulk solids.

The following interesting results were confirmed. (a) The rates of heterogeneous nucleation were tremendously increased by the presence of the template films, in particular the monostearin template film accelerated most remarkably. (b) As for the dependence on the difference in the chain length between the template and the guest, it was confirmed that the acceleration was solely observed when the chain length of the template was the same as or longer by 2 carbon atoms than the guest solute in the case of the fatty acid/alcohol combinations. No thorough study on the chain length dependence was examined yet for the monostearin/alcohol systems in the present study. (c) The molecular orientation of the template films was preserved in the heterogeneously nucleated guest crystals. The present results indicate the occurrence of hydrophobic heterogeneous nucleation of the *n*-alcohol crystals at the template/solution interface through van der Waals interactions operating in the lateral packing directions of the amphiphilic films.

Consequently, we present a new concept of heterogeneous nucleation of the organic substances from solution assisted by the vapor-deposited thin films through van der Waals interactions. This may make a contrast to the hydrophobic heterogeneity operating in the nucleation of inorganic crystals assisted by the amphiphilic films formed at an air-water interface (2).

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## 277.B6

### COOPERATIVE EFFECTS OF EXTERNAL ELECTRIC FIELD AND FIELD OF CHARGED NUCLEUS IN THERMODYNAMICS OF HETEROGENEOUS NUCLEATION

Shchekin A.K. and Warshavsky V.B.

*College of Physics, St. Petersburg State University, St. Petersburg, Russia*

An external uniform electric field is often used to separate positively and negatively charged condensation nuclei in experimental study of heterogeneous nucleation. In the axisymmetric electric field such as given by superposition of external uniform electric field and field of charged nucleus of condensation, the form of a liquid dielectric drop arising around the charged nucleus will differ from sphere. With fixed number of condensate molecules in the drop, the deviation of the equilibrium drop shape from spherical has an influence upon the value of condensate chemical potential and work of formation of the drop. The fact that the deviation is small allows us to apply an iterative method of simultaneous solution of the Laplace electrostatic equation and the equation for the drop shape obtained from the Laplace hydrostatic formula with allowance for deformation of the drop surface in the axisymmetric electric field. Using the condition of fixed drop volume at "turning on and turning off" the external electric field, we can derive a relationship for finding the condensate chemical potential in the drop. As a result, the equation for drop shape in the frame of reference where the drop is at rest, the condensate chemical potential, and the work of formation of the drop can be written as expansions in powers of a small parameter  $\epsilon$  which incorporates the cooperation effects of the external electric field and the field of charged nucleus. With the accuracy of the order of  $\epsilon^2$ , the drop shape is spheroidal with  $\epsilon$  playing the role of the eccentricity. With account of terms of the order of  $\epsilon^3$ , and  $\epsilon^4$ , the drop shape is already non-spheroidal. With the same accuracy, there are only terms of the order of  $\epsilon^2$  and  $\epsilon^4$  in expansions for the condensate chemical potential and for the work of drop formation, at this the contributions of the order of  $\epsilon^2$  are the same as for spherical drop whereas the contributions of the order of  $\epsilon^4$  depend on deviation from spherical drop. The presence of an external electric field leads to a decrease in the threshold value of the vapour supersaturation (above which the

condensation occurs as a barrierless process) and diminishes the height of the activation barrier of nucleation at vapour supersaturations lying below the threshold value. It is shown that dependent of charge sign contributions to the chemical potential of condensate in a drop and to the work of formation of a drop are absent in the approximation neglecting the excess surface polarisation. We investigated the stability to small axisymmetric disturbances of the drop shape for the drop formed around the charged nucleus and found the critical parameter separating stable and unstable states of the drop. The calculated drop shapes and the thermodynamic characteristics of nucleation in the external uniform electric field, which gives rise to such axisymmetric perturbation of the drop form, can be referred to both stable and unstable drops. With the accuracy up to terms of the order of  $\epsilon^2$ , the stable drop deforms into a prolate spheroid whereas the shape of the unstable drop represents an oblate spheroid.

## 278.B6 THE ROLE OF ADSORBED MONOLAYERS IN THERMODYNAMICS AND KINETICS OF CONDENSATION ON SOLUBLE NUCLEI OF SURFACTANTS

Shchekin A.K., Yakovenko T.M., Kuni F.M., Rusanov A.I.

*College of Physics, St. Petersburg State University, St. Petersburg, Russia*

The formation of an adsorbed monolayer is inevitable process associated with nucleation of a drop onto soluble surfactant nucleus out of supersaturated vapour. Usually, speaking about the role of surfactant monolayer at condensation or evaporation, one assumes the retardation effect of the monolayer concerned with the small value of the vapour condensation coefficient for the surface of the drop with dense surfactant monolayer. However, the state of the monolayer changes during the growth of a drop from a dense (condensed) monolayer to rarefied (gaseous) monolayer, with increasing the value of the condensation coefficient to the magnitude corresponding to the surface of pure condensate. The variation of the condensation coefficient on the stage of nucleation of drops has not previously considered in kinetics of condensation on soluble nuclei of surfactant. We have shown that there are three possible kinetic scenarios. If the point of monolayer transition from dense to rarefied state fits the sub-critical region in the axis of drop sizes, then the time of growth of nucleating drops up to this point increases (in comparison with the corresponding time for drops nucleating onto soluble nuclei of surface inactive substance). As a result, the characteristic time-lag, after which the super-critical drops appear with a regular nucleation rate, also increases. The nucleation rate itself changes at this insignificantly. If the point of monolayer transition fits near-critical region in the axis of drop sizes, then both the time of growth of drops up to lower boundary of the near critical region and the time require to surmount the activation barrier of nucleation increase whereas the nucleation rate decreases. Finally, if the point of monolayer transition appears in the super-critical region of drop sizes, then the time-lag increases and the nucleation rate decreases in proportion to the ratio of the condensation coefficient for the surface of pure condensate and that for the drop covered by a dense adsorbed monolayer of surfactant. Which kinetic scenario from considered above can be realised in practice for specified condensate and nuclei of specified surfactant depends on size of the condensation nuclei and on vapour supersaturation. The thermodynamic aspect of the effect of adsorption of surfactant matter of soluble nuclei on nucleation of drops is concerned with influence on the threshold value of vapour chemical potential above which condensation proceeds in a barrierless way. The adsorption of surfactant matter of a nucleus at the drop surface and formation of the monolayer turn to be stimulating vapour condensation on nuclei of rather small (submicron) size due to significant decrease in the threshold value of vapour chemical potential in comparison with condensation on soluble nuclei of surface inactive matter. The situation reverses for nuclei of larger (micron) size. Finally, for nuclei of much larger size (over micron), the thermodynamic influence of the adsorption of a surfactant matter of the nuclei becomes practically insensible (whereas the presence of a dense monolayer on the stage of nucleation of drops will continue play the role in condensation kinetics and will be exhibited through the characteristic times of the process).

## 279.C1 AGGREGATION OF SILICA PARTICLES UNDER EFFECT OF DEPLETION FORCES IN THE EXCESS OF NONIONIC SURFACTANT

V. L. Alexeev

*Petersburg Nuclear Physics Institute, 188350, Gatchina, Russia*

In recent years many investigations in the field of colloid science have been devoted to systems with attractive particle interactions, since to govern the attractive potential means to govern stability of colloids. It has been shown [1] that excess surfactant such as Triton X100 in the bulk phase of silica sol has strong consequences on the thermodynamical behaviour of silica particles. Forces resulting from the pressure of excess micelles in the aqueous solutions and pushing the colloidal particles into direct contact has been called the <<depletion forces>> [2].

Depletion flocculation was observed for Triton X100-silica mixtures containing an excess of the surfactant i.e., when the amount of Triton X100 was higher than it is necessary for complete coverage of silica particles. After short time of storage (about 3 weeks) such the mixtures exhibit progressive aggregation of silica particles, sedimentation of aggregates and, at last, phase separation. Thus, this depletion flocculation leads to a phase transition which can be characterized as fluid-solid transition.

Semiquantitative analysis of the experimental phase diagram with the help of Bibette's approach [2] shows that depletion attraction exerted by excess surfactant is responsible for irreversible aggregation of silica particles.

1. V. L. Alexeev et al. // *Langmuir*, 1996, 12, 2392.

2. J. Bibette et al. // *J. Phys. II France*, 1992, 2, 401.

## 280.C1 VERTICAL STRATIFYING FILMS: PROOF OF THE HEXAGONAL PARTICLE STRUCTURING AND STRATIFICATION WITH CYLINDRICAL MICELLES

E. S. Basheva and P. A. Kralchevsky

*Laboratory of Thermodynamics and Physicochemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

Vertical macroscopic foam films formed from micellar solution of ionic and nonionic surfactants or latex suspensions exhibit a series of parallel, coloured horizontal stripes of different thickness, whose width gradually increases with time. The stepwise profile of such "stratifying" films can be explained [1] by the existence of an ordered structure of colloidal particles inside the film. The stratification is interpreted as a layer-by-layer thinning of that structure. In spite of the fact that there are many *indirect* proofs of the particle structuring inside stratifying films, a *direct* observation of the structuring is missing so far. To elucidate this point we studied the step-wise thinning of vertical foam films formed from suspensions of monodisperse latex spheres. We applied a method originally developed for wetting films [2]. By measuring the light wavelengths at which the reflectance from two neighbouring steps coincide, we established that the particle multilayers inside the film have hexagonal packing.

Not only the film thickness, but also the force exerted on the frame (in which the vertical film has been formed) exhibits step-wise changes in the process of film stratification. We measured the changes in the force by means of a precise balance and from the data we calculated the contact angles between the film stripes and the Plateau border. The experimentally determined contact angles agree well with the theory [3] of the oscillatory structural forces in the stratifying films.

In addition to the above experiments with films containing *spherical* colloid particles, we observed stratification also with films formed from surfactant solutions containing *long cylindrical* micelles. The thickness of the metastable states of the stratifying films and final equilibrium thicknesses have been interferometrically measured. In the case of cylindrical micelles the step-wise changes in the film thickness turn out to be of the order of the cylinder diameter which implies that the rod-like micelles are oriented parallel to the film surfaces.

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## 281.C1

### STABILITY OF COLLOIDAL SUSPENSIONS:

#### A DLVO-TREATMENT ACCOUNTING FOR SURFACE HETEROGENEITIES

H. Behrens, M. Schudel, M. Semmler, M. Borkovec, P. Schurtenberger, H. Sticher

*Institute of Terrestrial Ecology, Federal Institute of Technology (ETH) Zurich, Grabenstrasse 3, CH-8952 Schlieren*

Colloidal aggregation is commonly described in the framework of the classical theory by Derjaguin, Landau, Verwey and Overbeek (DLVO). This theory fails, however, in predicting quantitatively the aggregation rate constants in the slow regime, overestimating their dependence both on the electrolyte concentration of the solution and on the particle radius by many orders of magnitude. Various approaches have been proposed to overcome these well-known discrepancies between theory and experiment, for example by including the concept of surface roughness or of heterogeneity in the surface properties. Not much theoretical work has been published, however, about pH-dependent aggregation, only few experimental results being reported in the literature.

In our work, we used photon correlation spectroscopy to investigate on suspensions of well characterized, monodisperse latex spheres and on hematite suspensions of different morphology. Stability was measured as a function of pH for different ionic strengths and particles of different size. The charging behaviour was observed using acid-base-titrations, while electrophoretic measurements were applied to determine the zeta potential of the particles. Gas adsorption was used to characterize their surface area, the size distribution was assessed by transmission electron microscopy. For a theoretical discussion of our experimental findings, a DLVO-type calculation based on the solution of the full nonlinear Poisson-Boltzmann equation was combined with charge regulation models and a strategy to include the effects of surface heterogeneities.

## 282.C1

### SURFACE FORCES IN FOAM FILMS STABILIZED WITH ZWITTERIONIC PHOSPHOLIPIDS

R. Cohen<sup>1</sup>, D. Exerowa<sup>1</sup>, T. Yamanaka<sup>2</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*Laboratory of Chemistry, Faculty of Education, Chiba University, Inage-ku, Chiba 263, Japan*

A detailed analysis of surface forces in foam films stabilized with zwitterionic phospholipids is carried out. The data obtained from studies of foam films formed from aqueous solutions of palmitoyllysophosphatidylcholine (lysoPC) and lauroyllysophosphatidylethanolamine (lysoPE) and from liposome suspensions of dimyristoylphosphatidylcholine (DMPC) are considered. Some general inferences on the nature of surface forces and conditions for transition between long- and short-range intermolecular forces are made. The thin liquid film microinterferometric method of Scheludko and Exerowa and the pressure-balance technique are employed to experimentally determine foam film thickness as a function of electrolyte concentration ( $C_{el}$ ) and to directly measure the disjoining pressure / thickness ( $\Pi(h)$ ) isotherms in the presence of mono- and divalent ions. In all cases at low NaCl concentrations silver films are obtained that decrease in thickness with increase in  $C_{el}$  until Newton black films are obtained. The obtaining of thick equilibrium films at low  $C_{el}$  is evidence of the action of electrostatic repulsive forces in the film. Film thickness dependence on phospholipid concentration is found. Direct measurement of  $\Pi(h)$  isotherms for films stabilized with DMPC and lysoPE show a barrier-like transition to Newton films. Experimental isotherms are compared with the DLVO theory equations showing that electrostatic repulsion under the conditions of constant charge is operative. To get more of an insight in the mechanism of formation of surface charge and potential at the film/air interfaces the effect of the pH of the solution on  $h$  is studied and

isoelectric states at the film interfaces are found similarly to previously reported results obtained with foam films stabilized with synthetic non-ionic surfactants.

In the case of  $\text{CaCl}_2$  added  $\text{Ca}^{2+}$  ion binding leads to a Newton to silver film transitions for the films stabilized with lysoPC and to common black films in the case of lysoPE. The transitions indicate a change of the type of surface forces stabilizing the film from short-range to long-range electrostatic repulsive ones. The effect of the specific adsorption of the positive  $\text{Ca}^{2+}$  on surface forces is examined. The comparison between the transition concentrations in the case of foam films stabilized by lysoPC and lysoPE with  $\text{CaCl}_2$  added demonstrates the effect of the polar head-group structure on  $\text{Ca}^{2+}$  binding. The results compare well with data obtained from other phospholipid membrane systems.

## 283.C1 SURFACE FORCES IN MICROSCOPIC FOAM FILMS FORMED FROM NATURAL LUNG SURFACTANT EXTRACTS

R. Cohen<sup>1</sup>, D. Exerowa<sup>1</sup>, Z. I. Lalchev<sup>2</sup>, R. K. Todorov<sup>2</sup>

<sup>1</sup>*Inst. of Physical Chemistry, Bulg. Acad. of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*Dept. of Biochemistry, Faculty of Biology, Sofia Univ., Sofia 1421, Bulgaria*

Surface forces in microscopic horizontal foam films formed from aqueous solutions of porcine lung surfactant (LS) are studied by measuring equilibrium film thickness ( $h$ ) as a function of NaCl concentration ( $C_{\text{el}}$ ) and by direct measurement of disjoining pressure / film thickness ( $\Pi(h)$ ) isotherms. LS is isolated by a modification of the method of Ng et al. (V.L.Ng, K. Herndon, K. Mendelson, J. Snyder., *Biochim. Biophys. Acta*, 754 (1983) 218). The extraction is carried out according to Bligh-Dyer in  $\text{CCl}_4$  solution (E. G. Bligh, W. F. Dyer, *Can. J. Biochem. Physiol.*, 37 (1959) 911), followed by a liophilization procedure. The obtained LS sample consists mainly of phospholipids (DPPC (60 - 80%), phosphatidylglycerol (10%), and phosphatidylethanolamine (3-8%)) and 2-3% proteins.

Microscopic film thickness is measured in a wide range of  $C_{\text{el}}$ . It is found that unlike the microscopic films stabilized with individual phospholipids in this case  $h$  gradually decreases with increase in  $C_{\text{el}}$  from 95 nm at  $C_{\text{el}} = 5 \cdot 10^{-4} \text{ mol dm}^{-3}$  to 10 nm at  $C_{\text{el}} = 0.5 \text{ mol dm}^{-3}$ . These are the thinnest films observed and they do not change their thickness when increasing  $C_{\text{el}}$  to  $0.6 \text{ mol dm}^{-3}$ . The specific shape of the  $h(C_{\text{el}})$  curve indicates a non-barrier transition from long-range to short-range forces in these films. This conclusion is corroborated by the results of the direct measurement of the  $\Pi(h)$  isotherms carried out at different  $C_{\text{el}}$ . The comparison of the obtained experimental data with previous results obtained with foam films stabilized with individual phospholipids and with theory is evidence that besides the long range electrostatic repulsion other repulsive interactions are operative in the film as well. Further studies in this direction are needed to identify them and to elucidate their origin.

## 284.C1 SURFACE FORCES AND AQUEOUS FILM DRAINAGE BETWEEN A MERCURY DROP AND MICA

J.N. Connor, R.G. Horn and S.J. Miklavcic

*Ian Wark Research Institute, University of South Australia, The Levels, SA 5095, Australia.*

An experiment is described which is designed to measure surface and hydrodynamic forces between a mercury drop and a flat mica surface immersed in an aqueous medium. A variation of the FECO optical interference technique used in the Surface Force Apparatus allows measurement of the shape of the mercury drop as well as its distance from the mica, for various solution conditions and applied pressures. This enables a detailed exploration of the surface forces, particularly double-layer forces, between mercury and mica. A significant feature of the experiment is that the double-layer force can be varied by applying an electrical potential to the mercury.

Deformation of the drop under the influence of surface forces is an important factor, which in turn affects the overall interaction between the solid and the fluid. The deformation has been investigated theoretically by numerical solution of the Young-Laplace equation relating curvature of the mercury-water interface to the pressure difference across the interface, including the pressure due to surface forces between the mercury and the mica<sup>1,2</sup>. Predictions from this theoretical work will be compared to experimental data.



In addition to surface forces, it is also of interest to study hydrodynamic forces which affect the drainage rate of the aqueous film as the fluid drop approaches the solid surface. Our initial experiments have explored the conditions under which dimpling of the drop and formation of a barrier ring occur.

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## 285.C1

### STABILITY OF MAGNETIC COLLOIDS: ARE FERROFLUIDS EXAMPLES OF DIPOLAR FLUIDS ?

E. Dubois<sup>1</sup>, V. Cabuil<sup>1</sup>, R. Perzynski<sup>2</sup>, F. Boué<sup>3</sup>

<sup>1</sup>Université Pierre et Marie Curie, L.I.I.C. Groupe Ferrofluides, Casier 63,

<sup>2</sup>Laboratoire A.O.M.C., Casier 78, 4 place Jussieu, 75252 Paris Cedex 05, France

<sup>3</sup>L.L.B. CE Saclay, 91191 Gif sur Yvette, France, Laboratories associated to C.N.R.S.

Ferrofluids are colloidal dispersions of magnetic nanoparticles in a solvent. Stability of such dispersions is ensured by strong inter particles repulsions which counter-balance the Van der Waals and the dipolar magnetic interactions. In polar solvents, repulsions are electrostatic ones, due to particles surface charges. In oily solvents, repulsions are steric ones, due to adsorbed surfactant or polymeric species. Any modification in the interactions balance can induce destabilization of the dispersion. Intensive parameters as temperature or intensity of an applied magnetic field are used to monitor the stability of aqueous or non aqueous magnetic fluids. In both cases, repulsions have firstly to be decreased: by addition of an electrolyte in electrostatically stabilized systems, by addition of a bad solvent for sterically stabilized systems. Our results concern monodisperse magnetic nanoparticles dispersed either in water or in cyclohexane. Small Angle Neutron Scattering (SANS) experiments allow to observe the stable region and to approach the destabilisation thresholds. Temperature and magnetic field thresholds have been determined as a function of particles size, and some phase diagrams constructed. Aqueous and oily magnetic fluids will be compared and the results will be discussed in connection with the relevant theoretical works, especially those concerning dipolar fluids.

## 286.C1

### SELF-ASSEMBLED MONOLAYERS OF ALKANETHIOLATES ON THIN GOLD FILMS AS SUBSTRATES FOR SURFACE FORCE MEASUREMENTS. LONG-RANGE HYDROPHOBIC INTERACTIONS AND ELECTROSTATIC DOUBLE-LAYER INTERACTIONS.

Thomas Ederth<sup>1</sup>, Per Claesson<sup>1</sup>, Bo Liedberg<sup>2</sup>

<sup>1</sup>Laboratory for Chemical Surface Science, Department of Chemistry, Physical Chemistry,  
Royal Institute of Technology, S-100 44 Stockholm, Sweden

and Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden

<sup>2</sup>Laboratory of Applied Physics, Department of Physics and Measurement Technology,  
Linköping University, S-581 83 Linköping, Sweden

We report on the use of self-assembled monolayers (SAMs) formed by chemisorption of n-alkanethiolates ( $\text{HS}-(\text{CH}_2)_n\text{-X}$ ) on thin gold films as substrates for surface force measurements. Since the introduction of the Surface Forces Apparatus more than twenty years ago, the use of metal substrates in surface force measurements have not been extensive, mainly since the inherent roughness of polycrystalline metal films causes problems in the interpretation of surface force data. However, the roughness of vacuum-deposited films decreases as the film thickness is decreased, and we have used thin (10 nm) gold films deposited through evaporation onto flame polished glass substrates, giving surfaces smooth enough to make sensible interpretation possible. These surfaces were then further modified by self-assembly of alkanethiolates to provide the desired functionality to the surfaces.

The interest in this type of covalently bonded self-assembled structures has been growing rapidly in recent years, and their stability, the chemical flexibility provided by the possibility to functionalize the thiols before or after adsorption, and the ease with which they are prepared, makes them very attractive for use in



surface force measurements. Using mixtures of thiols would open the possibility to create surfaces with a wide variety of wetting properties, surface charge etc. Our aim is to take advantage of this evolution, and to use this type of surfaces in surface forces on a routine basis.

Results are presented from force measurements between thiol modified gold films in air, water, and aqueous solutions, using a non-interferometric bimorph surface force apparatus. Some problems of a more fundamental character associated with this type of systems, such as the influence of roughness and difficulties in calculating the van der Waals forces, will be discussed.

## **287.C1 A NOVEL TECHNIQUE FOR EVALUATION OF DLVO INTERACTION FORCES BETWEEN SMALL COLLOIDAL PARTICLES**

**Menachem Elimelech and Subir Bhattacharjee**

*School of Engineering and Applied Science, University of California, Los Angeles, CA 90095-1593, USA*

A novel technique, the surface element integration (SEI), has been developed to calculate the interaction energy and force between two surfaces of arbitrary shapes from the corresponding estimates of the interactions per unit area between two infinite flat plates. The underlying principle of the new technique relaxes the assumptions in the traditional Derjaguin's technique, and provides immensely improved estimates of the interaction energy. In case of a particle interacting with an infinite flat plate, SEI provides the exact interaction energy. The technique clearly demonstrates the salient contribution of the surface areas on the curved surface apparently not "seen" by the flat plate to the total interaction energy. This effect of hidden surfaces, when accounted properly in SEI, provides exact measures of the van der Waals and electrostatic double layer interactions between a sphere and a flat plate. An analytical expression for the van der Waals interaction energy between a sphere and a flat plate derived on the basis of the new technique is exactly similar to the expression derived by Hamaker using the volume integration approach. Estimates of the electrostatic double layer interaction energy and force obtained using SEI compared extremely well with the solutions of the Poisson-Boltzmann equation for a sphere-flat plate geometry using finite element and finite difference techniques. Analytical expressions for the electrostatic double layer interaction energy under conditions of constant surface potential and surface charge density, as well as using the linear superposition approximation have been derived using this technique. These analytical results are much simpler to use than most other approximate analytical expressions available for estimation of the interaction energy or force between two overlapping double layers, and they are exact. Comparisons of the electrostatic double layer interaction energy obtained using the new technique with other available results indicate that the latter methods (generally based on Derjaguin's approximation or the linear superposition approximation for spherical double layers) greatly overpredict the double layer interaction for small particles at low ionic strengths.

## **288.C1 MECHANISM OF NONIONIC POLYMER EFFECT ON AGGREGATIVE STABILITY OF COARSE SUSPENSIONS**

**Eremenko B.V., Malysheva M.L.**

*Taras Shevchenko University, Vladimirskaya Str.64, 252017 Kiev, Ukraine*

To clarify the mechanism of nonionic polymer adsorption effect on the stability of suspensions with micron particles, the complex investigation of adsorption of poly(ethylene oxide) (PEO) and its effect on electrostatic properties and stability has been performed. Samples of PEO with molecular masses from  $4 \cdot 10^3$  to  $2.2 \cdot 10^6$  and suspensions of silica, silicon nitride, silicon and titanium carbides were used.

It was found that adsorption of PEO decreases the surface charge density of silica and has no effect on the surface charge density of  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$  and  $\text{TiC}$ . At the same time it causes a decrease of the electrokinetic potential of particles owing to the shift of shear plane toward the solution. The calculated electrophoretic thickness of PEO adsorbed layers are in a good agreement with the dimensions of the end of tails of adsorbed macromolecules estimated from the Scheutjens-Fleer theory of polymer adsorption.

Experimental results on the coagulation of suspensions by electrolyte additions were compared with calculated potential energy curves of interaction of particles including Van-der Waals attraction, electrostatic repulsion, osmotic and volume restriction effects, estimated according Hesselink-Vrij-Overbeek theory in the approach of equal tails. All necessary molecular characteristics of adsorbed polymer layers were calculated according to the Scheutjens-Fleer theory on the base of experimental adsorption dates.

In the absence of electrolyte the stability of suspensions containing polymer of even the largest molecular mass is determined by electrostatic repulsion. Addition of electrolytes decreases the radius of electrostatic forces to the distances commensurate with the adsorbed polymer layer thickness. In this case suspension stability is determined by the balance of attraction and sterical repulsion forces and aggregation can take place in the secondary minimum only. Its depth depends on polymer molecular mass. With the increase of molecular weight of polymer the distances on which these minimums appear became larger and their depth decreases. In the presence of adsorbed layers of polymer of large molecular weights, the distances on which minimum appear are so large that attraction forces could not provide the depth of minimum enough for aggregation of the most large particles. The stabilization of suspensions takes place in that case.

When the molecular weight of polymer decreases, minimum shifts to the short distances and its depth becomes larger. More small particles could take part in aggregation process.

Beginning from the certain molecular weight the depth of minimum is enough for aggregation of even the smallest particles which present in suspension. In this case, sensibilization effect of polymer is observed. Coagulating concentrations of electrolyte are smaller than at the absence of polymer.

## 289.C1 THIN-FILM FORCES IN FOAM FILMS CONTAINING POLYELECTROLYTE AND SURFACTANT. DEPLETION AND STRUCTURING.

A. Espert, R. Klitzing, A. Asnacios, T. Hellweg, A. Colin, D. Langevin.

*C.R.P.P, C.N.R.S, Pessac, France*

Industrially, it has long been realized that the addition of polymers to a surfactant solution can significantly affect the stability of foams and emulsions. Typically when soluble polymers are added to the continuous phase, they increase the bulk viscosity which in turn can dramatically slow down the drainage of thin-liquid films and enhance the stability of the emulsion. More over, the addition of polymer to the continuous phase modify the single-interface properties as well as the interaction forces between the surfaces. These "surface forces" can be attractive or repulsive and depend on the nature and quantity of polymer adsorbed at the interface. Thus polymer are used as both flocculates and stabilizers.

Although there has been a lot of theoretical and experimental work on forces between mica surfaces there are only a few fundamental work reported on forces in thin liquid films containing polyelectrolyte and surfactants. Therefore, the objective of this work is to investigate the surface forces in single thin-liquid foam films made from solutions containing polyelectrolyte and surfactant.

To measure the surfaces forces we utilize a modified version of the porous plate technique, first developed by Mysels. The anionic polymer used in this study are a random -block copolymer (acrylamide-acrylamidesulfonate A.A.S) and a random polymere (polystyrenesulfonate P.S.S) with different molecular weight and different degree of charge. These polymers are studied in solution with cationic surfactant (dodecyltrimetyl amonium bromide) and ethoxylated non-ionic surfactant. For the range of concentration studied, the polymer chains form a transient network (semi-dilute regime) and no complex with the surfactant in the bulk.

At large separation, the force-distance profile is characterised by an attraction with two distinct regimes. The first one is the strongest and is attributed to complete depletion of polymers. As predicted by the theory, the range of the interaction is decreased as the concentration in polymer is increased. The second regime appears at further surface separations and at larger polymer concentration. Oscillatory forces indicative of polymer structuring are measured. It is suggested that the attraction results from an orientation depletion of the polymer network structuring by the surfaces. The oscillatory behaviour is further evidenced with measurement of the structure factor by light -scattering.

## 290.C1      TRANSITION FROM NEWTONIAN TO COMMON BLACK FILMS IN FOAM FILMS FROM EICOSAOXYETHYLENE NONYLPHENYL ETHER

D. Exerowa, R. Sedev, and R. Yankov

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

The dependence film thickness vs. surfactant concentration is monitored for microscopic foam films obtained from aqueous solutions of eicosaoxyethylene nonylphenyl ether, NP(EO)<sub>20</sub>, at constant electrolyte concentration (0.1 M KCl) and temperature (23 °C). A transition from bilayer (Newtonian black) film of thickness 9 nm to thicker Common black film starts in the range of  $(5.8 \div 7.0) \times 10^{-6}$  M NP(EO)<sub>20</sub>. This concentration range is very close to the concentration above which the bilayer film is thermodynamically stable according to the hole-nucleation theory [1]. The thickness gradually increases with surfactant concentration and close to CMC reaches 14 nm. This reflects the transition from short-range to long-range interaction - most probably steric in origin. Neither the slight variation in the capillary pressure ( $60 \div 40$  N/m<sup>2</sup>) with surfactant concentration nor electrostatic interaction (practically suppressed at 0.1 M electrolyte) can account for the effect observed.

The disjoining pressure vs. film thickness dependence was measured under the same conditions. All thicker films can be compressed to bilayer thickness at higher pressure -  $(1 \div 8) \times 10^4$  N/m<sup>2</sup>, and the pressure required significantly increases with surfactant concentration. The film thickness increases with surfactant concentration at any constant pressure (higher than the capillary pressure). The shape of the disjoining pressure isotherms also indicates that steric forces are probably responsible for the change in film stability from short-range (bilayer) to long-range (14 nm) interaction [2].

This is the first report of such a transition in foam films.

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## 291.C1      ABSORPTION AND FLUORESCENCE IN THE SURFACE FORCE APPARATUS

Torsten Grünewald<sup>1</sup>, Dirk Eck<sup>1</sup>, Christiane A. Helm<sup>1,2</sup>

<sup>1</sup>*Institut für Physikalische Chemie, Johannes Gutenberg-Universität, 55099 Mainz, Germany*

<sup>2</sup>*Fachrichtung Kristallographie, Universität des Saarlandes, 66041 Saarbrücken, Germany*

In the classical Surface Forces Apparatus (SFA), the interaction force between surfaces of a well defined geometry is measured as a function of distance, which is determined interferometrically. To obtain Å-resolution, the distance is measured automatically using a CCD-camera connected to a high resolution spectrograph. To obtain further information, the molecular thin layer between the surfaces is characterized spectroscopically, the absorption can be determined by using the field enhancement within an interferometer. To give an example, the surface forces across an aqueous dye solution are measured and correlated to the solute concentration. Dye adsorption onto the surfaces is accompanied by the occurrence of a short range repulsion. On increase of the dye concentration at the surfaces, first the van der Waals attraction disappears, and oscillatory forces with a periodicity corresponding to the diameter of the hydrated dye molecule appear. Eventually, the last dye layers trapped between the surfaces form a supersaturated solution, which leads to a short range repulsion until off-center crystallization occurs. However, the absorption technique relies on high dye concentrations. In contrast, fluorescence is a probe technique. We already succeeded to observe the lateral movement of a molecularly thin fluorescence-labelled polymer film in the SFA (7 Å thick, 0.3% of the monomer units labeled). Yet the implementation of the fluorescence technique in the SFA still needs further development, because one has to control stimulated emission.

## 292.C1 THE INTERACTION POTENTIAL BETWEEN COLLOIDAL PARTICLES IN SIMPLE FLUIDS

Douglas Henderson<sup>1,2</sup>, Stefan Sokolowski<sup>3</sup>, and Darsh Wasan<sup>2</sup>

<sup>1</sup>Department of Chemistry and Biochemistry, Brigham Young University, Provo UT 84602

<sup>2</sup>Department of Chemical Engineering, Illinois Institute of Technology, Chicago IL 60616

<sup>3</sup>Department for the Modelling of Physico-Chemical Properties, MCS University, 20031 Lublin, Poland

The classical DLVO theory predicts a relatively featureless curve for the interaction potential between colloidal particles in a fluid. The experiments of Israelachvili *et al.* have shown that, at small separations, the interaction potential becomes oscillatory, a behavior not predicted by the DLVO theory. Henderson has explained this effect by using the Percus-Yevick theory for hard sphere mixtures. However, the Percus-Yevick theory is known to be questionable in the limit of large particles in small concentrations. Henderson attempted to overcome this problem by using a hybrid of the Percus-Yevick and hypernetted chain approximations. In view of the *ad hoc* nature of Henderson's procedure, we have made some new calculations using more sophisticated theories and simulation methods. Our calculations show that Henderson's procedure is quite accurate. In this report, the results of some of these calculations as well as our experiments will be discussed.

## 293.C1 ADHESIVE FORCE OF COLLOIDS IN ELECTROLYTE SOLUTIONS EVALUATED BY AFM

Ko Higashitani and Kazushige Ishimura

Kyoto University, Chemical Engineering Department, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

The adhesive force of colloidal particles on a wall in liquids has been considered to be predictable by the equation of the van der Waals force between a particle and a plate. However, no systematic and reliable data of the adhesive force of colloids have been reported and so it is still unclear whether the equation is applicable to evaluate the adhesive force in solutions or not. The main reason why reliable data have not been obtained will be because the adhesive force depends on the local microscopic structure of the surface of the particle and plate, such as the structure of water molecules, ions and hydrated ions adsorbed on the surface, which has not been clarified until the Surface Force Apparatus (SFA) and Atomic Force Microscope (AFM) were utilized.

Here the AFM (Nano-Scope III of Digital Instruments Co.) is used to analyze the microstructure of the adsorbed layer on the surface and also to measure on the molecular level the adhesive force between a particle and a mica plate in electrolyte solutions of LiCl, NaCl, KCl and CsCl whose cations are monovalent but are different in hydration enthalpy. The following results are obtained from the comparison between the microstructure of the surface and the adhesive force.

(1) The adhesive force between surfaces in electrolyte solutions depends on the contact time of the particle on the surface, the electrolyte concentration and the hydration enthalpy of cations.

(2) The adhesive force is closely related with the structure of the adsorbed layer of cations and water molecules on the surface, that is, the strong adhesive force is obtained when highly hydrated cations are adsorbed to form a thick but weak adsorbed layer, while the weak adhesive force is observed when poorly hydrated cations are adsorbed to form a thin but strong adsorbed layer.

**294.C1****RESEARCH ON THE COLLOID MATERIALS FOR  
STOPE STABILITY SIMULATION****Wan Hong, Zhao Hongzhong***Department of Resources and Environmental Engineering, Wuhan University of Technology,  
Wuhan, P.R. China*

Applying statistics and the orthogonal experiment design method, this paper studies the colloid materials for stope stability simulation and gets some material blending ratios to meet demands of original models to obtain satisfactory reliability.

**295.C1****ELECTROSTATIC INTERACTIONS BETWEEN TWO IDENTICAL  
THIN DISKS OF ARBITRARY ORIENTATION IN AN ELECTROLYTE SOLUTION****Jyh-Ping Hsu and Ming-Tsan Tseng***Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617 RO.C*

The electrostatic interactions between two identical, infinitesimally thin, charged disks in an electrolyte solution are investigated. The charged entities can assume an arbitrary orientation in space, and their surfaces are remained either at constant charge density or at constant potential. We show that if the surface potential is low, the governing Poisson-Boltzmann equation (PBE) can be solved analytically for the former. A boundary collocation method is adopted to solve the PBE for the latter. The interaction energies of the system under consideration including the electrostatic repulsive energy and the van der Waals attractive energy are estimated. We found that, for a fixed center-to-center distance between two disks, these energies are at maximum if they are on the same plane, and at minimum if they are in an opposite position. The difference between the maximal and the minimal electrical repulsion energies increase with  $kr_0$  for both constant surface charge and constant surface potential,  $k$  and  $r_0$  being, respectively, the reciprocal Debye length and the radius of a particle. That for the van der Waals attraction energy follows the same trend.

**296.C1****SPREADING AND DETACHMENT OF ORGANIC DROPLETS  
AT AN ELECTRIFIED INTERFACE****Nadica Ivosevic and Vera Zutic***Center for Marine Research Zagreb, Ruder Boškovic Institute Zagreb, Croatia*

We investigate adhesion and spreading of organic particles at aqueous/mercury electrode interface where the attractive surface forces are controlled by applied potential. Effect of potential on spreading and detachment was investigated by observing the shape of n-hexadecane droplet at the mercury pool/aqueous electrolyte interface. Mercury electrode surface is atomically smooth, fluid and chemically inert, surface charge densities and interfacial tensions are well known; the critical interfacial tension of wetting can be determined experimentally (1).

Attachment of droplets depends on applied potential and reflects wetting equilibrium as a results of interfacial forces at the three boundaries and buoyancy. Microdroplets, after attachment spread instantaneously to a film at the mercury/aqueous electrolyte interface, while a larger droplet ( $d=5$  mm) assumes a planar convex lense shape. By sweeping potentials beyond the critical value of wetting, the droplet shape changes from lense through ideal sphere to an elongated shape with decreasing contact area. The new shape established instantaneously upon changing potential. The change of droplet shape is reversible and could be repeated many times. At a constant potential the shape of droplet remain stable over infinite period of time. Detachment of droplet (by buoyancy) takes place only when the applied potential exceeded the critical wetting potential (1) by one volt. The corresponding critical interfacial tensions of wetting and detachment of hexadecane differ by  $68 \text{ dyn/cm}^2$ . The experimental difference could be interpreted as an effect of modification of die mercury/aqueous electrolyte interface by a monolayer of n-hexadecane molecules similar to recently reported behaviour of gold modified electrodes (2,3).

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**297.C1****SHEAR PROPERTIES OF MOLECULARLY  
CONFINED LIQUID CRYSTALS****Joanna Janik<sup>1,2</sup> Rafael Tadmor<sup>1</sup> Jacob Klein<sup>1</sup>**<sup>1</sup> *Weizmann Institute of Science, Department of Materials and Interfaces, Rehovot 76100 Israel*<sup>2</sup> *Institute of Physics, Jagiellonian University, ul. Reymonta 4, Cracow, Poland*

Using a surface force balance [1], the orientation of a nematic liquid crystal (6CB) confined between mica surfaces, and its response to shear under extreme confinement was examined. By simultaneous measuring of the force and the refractive index profile, we were able to distinguish between planar, planar twisted and homeotropic orientation of the nematic [2]. When the mica was exposed to air for short periods (< 1 hour) prior to introducing the 6CB, either planar or twisted planar orientations resulted, depending on the relative orientation of the mica axes. For longer exposure periods ( $\geq 3$  - 4 hours) prior to introducing the nematic, a homeotropic orientation was observed, presumably because the mica surfaces became sufficiently hydrophobised. Slow transitions (over a period of days) from a planar twisted to a planar orientation, and from a homeotropic to a planar orientation could be observed in certain conditions. We propose that these are associated with anchoring transitions on the mica surfaces, resulting from adsorption of water molecules penetrating by diffusion from the ambient atmosphere. Shear forces and normal forces were measured in a nematic phase. The dependence on the orientation of confined liquid crystal response to shear was investigated.

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2. Joanna Janik, Rafael Tadmor, Jacob Klein, in press

**298.C1 THE AFM STUDY OF INTERACTION FORCE BETWEEN SPHERICAL  
SILICA PARTICLE AND MICA PLATE IN ALCOHOL-WATER SOLUTIONS****Yoichi Kanda and Ko Higashitani***Dept. of Chem. Eng., Kyoto University, Kyoto, Japan*

The colloidal particles in non-aqueous solution are widely treated in many important technological processes. The quality of the products, for example, depends on the stability of the particles in the manufacturing process and the understanding of the surface force, which is the crucial factor for the stability, is very important for the control of the quality. The mechanism of surface forces in nonaqueous solutions were investigated by a few researchers [1] and it is not systematically understood yet. In order to clarify the difference from aqueous systems, the Atomic Force Microscope (AFM) was used to measure *in-situ* the long-range and short-range interaction forces and adhesive forces between mica plate and spherical silica particle (or tip apex) in alcohol-water solutions on the molecular level. The following results were obtained:

(1) Long-range interaction force: The long-range interaction force is successfully expressed by the DLVO theory at  $C_{alc} < 70$  wt% and the variations of the apparent surface potential with the alcohol concentration are explained by the ion association mechanism proposed by Fuoss [2].

(2) Short-range interaction force: A step-like interaction force shown in Fig. 1 are found at  $C_{alc} > 90$  wt% and it is considered to the vertical adsorption of alcohol molecules.

(3) Adhesive force: The adhesive force decreases with the alcohol concentration because of the change of the Hamaker constant with medium property, but the big attractive force was observed at  $C_{alc} = 90$  wt% especially in n-propanol. This big adhesive force is explained by a mechanism that the water-rich space around the contact point of two surfaces is formed such that the bridging force acts between the surfaces.

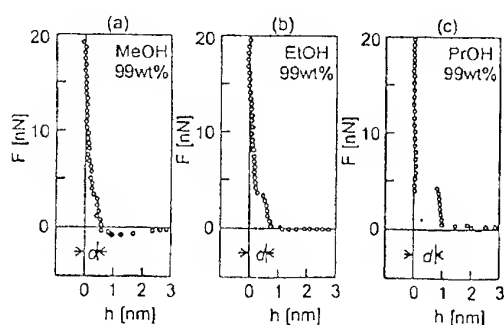


Fig. 1 The short-range interaction force between the probe apex and mica for various kinds of alcohol

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2. R. M. Fuoss, *J. Am. Chem. Soc.*, 80 (1958) 5059.

## 299.C1

### PROBING THE MECHANISMS OF CERAMIC DISPERSANTS USING AN AFM

A. U. Khan, P. F. Luckham and S. Manimaaran

*Department of Chemical Engineering and Chemical Technology,  
Imperial College of Science Technology and Medicine, London SW7 2BY, UK*

Quality ceramic processing requires favourable system interactions so as to minimise cost and maximise ease of manufacture. In the absence of dispersants or deflocculants such a condition is not easily achieved, as the attractive forces present between particles can lead to flocculation when introduced into solution. Stability can however be imparted by way of steric or electrostatic effects, and their success at doing so has traditionally been investigated at a macroscopic level using well established methods such as rheology. Although the success of these studies are beyond question they do have one shortcoming - they do not provide us with a definitive view describing the interactions at a particulate level. The work presented here attempts to address this point by investigating the nature of the interactions between particles by making use of a relatively new tool - the Atomic Force Microscope (AFM). The AFM is currently the best tool available allowing us to mimic the interactions that may occur between two particles.

In the case of this study Darvan C, a polyelectrolyte, and Aluminon, a dispersant, have been investigated under a variety of conditions so as to gain a more complete understanding of their actions as dispersants. In the case of Aluminon, the actions of a binder, PVA, has also been investigated so as to gain further insight into the modification of inter-particle interactions by the additional presence of a binder. Rheological data retrieved from a Bohlin rheometer are compared with data obtained at a nano scale using a Topometrix Explorer AFM.

## 300.C1

### FOAM FILMS FROM A CATIONIC SURFACTANT: DLVO AND NON-DLVO INTERACTIONS

T. Kolarov, R. Yankov, D. Exerowa

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

The porous plate technique that permits direct measurements of interaction force vs. film thickness (the disjoining pressure isotherm) is used to study films from a cationic surfactant. The aim is to estimate the features of the interaction behaviour in these type of systems. The experiments are performed with microscopic foam films from aqueous solutions containing  $0.5 \text{ mmol/dm}^3$  cetyltrimethylammonium bromide (CTAB) over a wide range of NaBr concentrations ( $0 - 0.3 \text{ mol/dm}^3$ ). A reliable triple-layer model is adopted for the films and the effective planes of origin of both Van der Waals and double-layer forces are identified. The variation of the interaction forces within the range of  $0 - 0.02 \text{ mol/dm}^3$  NaBr are found to be in accordance with the predictions of the DLVO theory. The dominating force is the double-layer repulsion. A fit between the experiment and the theory yields reasonable values for both the Debye length and diffuse

double-layer potential. Starting from  $0.02 \text{ mol/dm}^3$  NaBr the experimental data are found to be in increasing discrepancy with the DLVO theory. The total force seems to be less repulsive than expected from the DLVO theory. The back and forth shift of the disjoining pressure isotherms under increasing NaBr concentration occurs at significantly thicker films and lower pressures than those predicted by the DLVO theory. It is concluded that the interaction behaviour of the system studied clearly indicates that DLVO forces are operative below  $0.02 \text{ mol/dm}^3$  NaBr while above this concentration non-DLVO forces should also be considered. As regards a further identification and separation of these non-DLVO forces, the reliable theoretical assessment of DLVO forces at high electrolyte concentrations seems to be of primary importance.

### 301.C1 THE INFLUENCE OF SOME NORMAL ALCOHOLS UPON THE COAGULATION KINETICS OF THE STARCH DISPERSIONS

I.P. Lychkin, R.M. Jasunas, I.N. Afinogenova, G.P. Remisov, V.S. Shein.

*Voronezh State Technology Academy, Voronezh, Russia*

Lyophilic dispersion system is formed at definite conditions in the system: potato starch - water. Particles stabilization of the disperse phase in such system is carried out by definite structure formations from the water molecules on the boundary line of phases. Any phenomenon increasing this formation will contribute to system stabilization. At the opposite action the system becomes to some extent unstable. One can trace such influence by the kinetics of the dispersion system changes.

Thus, from the theoretical point of view the kinetics of coagulation is the key to understanding of the system stabilization mechanism, from practical - the lever for system controlling in the interests of practical purposes.

There have been obtained coagulation isotherms of starch dispersions by methyl, ethyl and normal propyl alcohols at different concentrations in coordinates: average radius of particles - time.

The task was to find out analytical expression for the isotherm of the coagulation kinetics. Having suggested that

$$\lim_{t \rightarrow \infty} r = r_{\infty} = \text{const}$$

we came to the conclusion that  $r$  should be used as  $r^3$  because mass concentration is used with the last.

$$\frac{4}{3} \pi r^3 \rho v = \text{Con}_k \quad (1)$$

$\rho$  - substance density of the dispersion phase,  $v$  - partial concentration,  $\text{Con}_k$  - mass concentration of dispersion particles.

As the analysis shows the experimental data can be approximated by the equation :

$$y = y_{\infty} \frac{t}{\alpha + t} \quad (2)$$

where  $y = r^3 - r_0^3$ ,  $r_0 = r/t \rightarrow 0$ ,  $y_{\infty} = r_{\infty}^3 - r_0^3$ ,  $r_{\infty} = \lim_{t \rightarrow \infty} r$ ,  $\alpha$  - constant in isothermal conditions. Evaluation of destabilization phenomenon can be carried out by means of coagulation rate  $C_o$ , disaggregation  $C_{d_o}$ .

These constants are derived from the equation of the coagulation kinetics (3)

$$\frac{-dv}{dt} = C_v^2 - C_d v \quad (3)$$

It has been proved that equation (2) is the solution of the equation (3).

Dependences  $C_o$  and  $C_{d_o}$  on the number of methyl groups in carbon hydride radical  $n_{CH_2}$  at different concentrations of alcohol in the system differ greatly. This attracts one's attention.

Complicated character of the underlined dependences is due to a large number of factors affecting  $C_o$  and  $C_{d_o}$  in the process being studied.

Thus, in principal one can not say about decreasing or increasing constants of the coagulation process in dependence on  $CH_2$  at any concentration range of the destabilizing alcohol.

Such conclusions can be made only for several regions in which  $C_o = C_o(n_{CH_2})$ ,  $C_{d_o} = C_{d_o}(n_{CH_2})$  have the character of monotonous decrease or increase.



### 302.C1 ORIENTING POTENTIAL AND ITS ESTIMATION TECHNIQUE FOR A WIDE CLASS OF ORGANIC LIQUIDS

Matveenکو V.N., Levchenko V.A.

*Department of Chemistry, Moscow State University, 119899 Moscow, Russia*

The basic experimental data obtained in the newest investigation of the molecule liquid structure at the boundary interface with the solid surface are that thanks to its specific orientational order in molecule arrangement the liquid boundary layer has been distinguished into a particular epitropic type of liquid crystals.

In terms of the technique developed earlier [1] and the preliminary research of the behavior of the lutidine heat anomaly in the bulk with the developed surface [2-3] we have calculated the experimental dependence of the optical phase difference  $\sigma$  on the temperature for a number of organic liquids. It is given in fig.

The qualified estimation of orienting potential  $G$  of the quartz surface for lutidine  $0.62 \times 10^4 \text{ J/m}^2$  has been made on the basis of the above calculation.

Besides, the further analysis of this calculation showed the methodology of the orienting potential estimation proposed in [1] could be also used for a wide class of organic liquids.

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### 303.C1 THE STABILITY AND THE ELECTROSURFACE PROPERTIES OF THE AQUEOUS DISPERSIONS OF THE OXIDIZED GRAPHITE AND DIAMOND

V.N. Moraru, D.V. Moraru, F.D. Ovcharenko

*Institute of Biocolloidal Chemistry, National Academy of Sciences of Ukraine,  
42 Vernadsky blvd, 252142 Kyiv, Ukraine*

The dependencies of the electrokinetic potential ( $\zeta$ ), the surface charge density ( $\sigma_s$ ), and the optical density ( $D$ ) of the oxidized graphite (OG) and oxidized synthetic diamond (OSD) suspensions on the KCl, BaCl<sub>2</sub>, YCl<sub>3</sub> concentration and the medium pH have been investigated.

The quantitative analysis of these dependencies has allowed to obtain a new information concerning the mechanism of the origin and the charge value, surface group dissociation constants and the connection between the object acidic-basic and electrosurface properties.

The revealed deviations from the Schulze - Hardy rule, the phenomenon of the reverse dispersion coagulation in an acidic medium as well as the maximum in the  $\zeta = f(C_{KCl})$  curves in the region of the values  $\chi_a \approx 100$  where the influence of the DEL polarization is little neglected can be explained only by the existence of the hydrated boundary layer (HBL) on the disperse particle surface. The character of the change in the dependencies of  $\zeta$ ,  $D = f(C_{KCl})$  and  $\zeta$ ,  $D = f(pH)_{j=const}$  for the OSD sample after annealing as well as the carried out calculations of the potential curves of the pair interaction between the OSD and OG particles within the generalized DLVO theory with the account of the structural forces convincingly confirm a substantial contribution of the HBL in providing the stability of the systems under investigation.

The whole complex of the carried out investigations and calculations has shown that the decisive HBL contribution in the stability of dispersions is limited by the region of the acidic pH and high electrolyte concentrations, whereas at pH >7 and electrolyte concentrations below the coagulation threshold, the aggregative dispersion stability is provided preferably by the electrostatic factor.

## 304.C1

## THE ROLE OF ADSORPTION IN COLLOIDAL INTERACTION

H. J. Müller

*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Berlin-Adlershof, Germany*

The interaction between two surfaces of a liquid, for example in a thin liquid film, changes the chemical potential of the surfactant in the surface excess phase (SEP) of the film. In the case of strong interaction and very thin films this leads to a significant amplification of the known DLVO interaction forces [Müller "On the contribution of changing adsorption to the disjoining pressure in thin liquid film", submitted to J. Phys. Chem. 1]. A theory that takes into account these effects predicts (i) an increase of adsorption in the case of attractive forces between the film surfaces and (ii) an desorption of surfactant molecules in the case of repulsive disjoining pressure. The dependence of the adsorption density  $\Gamma_i$ , on disjoining pressure  $\Pi(h)$  and the surface tension  $\sigma$  (bulk solution) is given by

$$\Gamma_i(h) = \Gamma_i(\infty) \exp \left\{ \frac{(\sigma - \sigma^o)(Z - 1)}{RT\Gamma^\infty} \right\}, \text{ with } Z = \frac{TS^{so} + \sigma^o}{TS^{so} + \sigma^o + \Psi / 2 + \Pi\delta} \text{ and } \Psi = \int_h^\infty \Pi(h')dh',$$

( $\Gamma_i(\infty)$ : adsorption at the surface of an infinite thick film,  $\sigma^o$ : surface tension of pure water,  $R$ : gas constant,  $T$ : Temperature,  $\Gamma^\infty$ : saturation adsorption (for instance from fitting the measured  $\sigma(\ln C)$  dependence to a Langmuir isotherm),  $S^{so}$ : surface excess entropy,  $\delta = v\Gamma^\infty$ ;  $v$ : molar volume).

The part of the whole interaction energy caused by the change of the adsorption is given by:

$$\Delta\Lambda_{uds} = \left( \frac{\partial \sigma^f}{\partial \Gamma_i} \right)_h \Delta\Gamma_i + \sum_i \mu_i \Delta\Gamma_i \text{ with } \Delta\Gamma_i = \Gamma_i(h) - \Gamma_i(\infty). \text{ For } \left( \frac{\partial \sigma^f}{\partial \Gamma_i} \right)_h \text{ the value at } h = \infty \text{ is taken}$$

from the adsorption isotherm.

Beside the excess of matter, other excess quantities are influenced by the interaction of interfaces as well. The mutual influence of the excess quantity and the interaction force then may lead to an essential modification of the interaction force, as well. In this context we consider the following model of adsorption of H-bonds: The density of H-bonds is increased above its value in the volume in a layer very near a interface of water with a hydrophobic medium. This H-bond excess may be due to minimizing the surface free energy. The validity of this postulate is supported by physical reasoning and by some experimental results and simulations of aqueous interfaces. Comparable to the surfactant excess, varied by the interaction of the interfaces, also the H-bond excess is modified by the same mechanism. This results for a water film between hydrophobic walls in an additional attraction stronger as van der Waals interaction. This additional attraction can be identified with the often observed "long-range hydrophobic attraction", discussed controversially until now.

In the case of wetting films the same model should result in a films thicker then expected from Lifshitz theory of dispersion forces due to amplification of the repulsive van der Waals force in the wetting film. Such an effect was observed by Pashley and Kitchener [J. Colloid Interface Sci. 71(1979), 491] and recently by Panella et al. [Phys. Rev. Lett. 76 (1996), 3606].

In the case of interaction of two aqueous surfaces across a vapour filled gap a weakening of the interaction force was predicted by the theoretical approach given here.

## 305.C1

## DEVELOPMENT OF THE PARTICLE SCATTERING APPARATUS FOR PROTEIN-STABILISED EMULSION DROPLETS

Brent S. Murray, Joseph M. McCarney and Eric Dickinson

*Food Colloids Group, The Procter Department of Food Science, The University of Leeds, Leeds LS6 9JT, UK*

We have developed a further version of the particle scattering apparatus (PSA) originally due to van de Ven *et al.*<sup>1</sup> The basis of the instrument remains the same and consists of two glass plates which move exactly parallel to one another to create a laminar shear field. The interaction between a particle fixed on one of the plates and a mobile particle between the plates is observed via a microscope. From the initial and final trajectories of the mobile particle, i.e., before and after "scattering" by interaction with the fixed particle, one

can in principal calculate the particle interaction force as a function of interparticle separation. The improved apparatus consists of two larger and more rigid plates with facilities which allow for extremely accurate and easy alignment of the plates to maintain them parallel over large distances (relative to particle sizes of a few microns). The lower plate can be driven over a wide range of speeds very accurately by a highly geared down and damped stepper motor drive. In addition, particle co-ordinates are tracked in real time (up to 25 per second) with no need for separate frame by frame analysis to locate particle centres.

Results will be presented for collisions between polystyrene latices with and without added protein as adsorbent and for protein-stabilised emulsion droplets. Comparison will be made with the expected form of the particle collisions predicted from simple theory.

I. van de Ven, T. G. M., Warszynski, P., Wu, X. and Dabros, T. *Langmuir* 1994, 10, 3046-3056.

### 306.C1 INFLUENCE OF PEO-PPO-PEO COPOLYMERS ON THE SURFACE FORCES IN FOAM FILMS FROM BSA

Zs. Németh<sup>1</sup>, R. Sedev<sup>2</sup>, R. Ivanova<sup>2</sup>, and D. Exerowa<sup>2</sup>

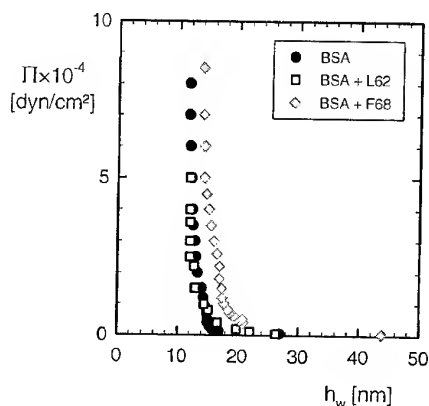
<sup>1</sup>Physical Chemistry Department, Technical University of Budapest, H-1521 Budapest, Hungary

<sup>2</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Proteins molecules adsorb at the liquid/air interface. Their foaming properties are of primary importance in many industrial processes. In this study we report the disjoining pressure in foam films from BSA and its modification upon addition of PEO-PPO-PEO copolymers.

The dependence of the surface force on film thickness is monitored by the porous plate method. The disjoining pressure isotherm obtained with BSA (4 g/L) is shown below. The disjoining pressure monotonously decreases with film thickness. At pressure higher than  $2 \times 10^4$  dyn/cm<sup>2</sup> a constant modulus of elasticity is found ( $5 \times 10^5$  dyn/cm<sup>2</sup>).

As can be seen the addition of L62 (EO<sub>9</sub>PO<sub>30</sub>EO<sub>9</sub>) has negligible influence on both the shape and location of the isotherm. However film rupture occurs at about  $5 \times 10^4$  dyn/cm<sup>2</sup>. Addition of F68 (EO<sub>76</sub>PO<sub>30</sub>EO<sub>76</sub>) shifts the isotherm to the right, the effect being more pronounced at lower pressure. Since experiments are conducted at pH = 5.2 (BSA's isoelectric point) the influence of electrostatic interaction should be negligible.



Given the asymmetry of the two pluronics, a simple explanation can be outlined as follows. Both pluronics adsorb onto the BSA molecule. The effective molecule dimensions are practically unchanged for L62 but increased for F68 - because of the longer PEO chains. This reflects in the shift of the isotherm observed.

Convergence of the isotherms at higher pressure shows that the BSA elastic response is stiffer than that of PEO. Indeed the modulus of elasticity is lower ( $2.5 \times 10^5$  dyn/cm<sup>2</sup>) and coincide with values reported for similar Pluronics.

### 307.C1 THE HYDRATION REPULSION BETWEEN CHARGED SURFACES AS AN INTERPLAY OF VOLUME EXCLUSION AND DIELECTRIC SATURATION EFFECTS

V. Paunov<sup>1</sup>, R. Dimova<sup>1</sup>, G. Broze<sup>2</sup>, and A. Mehreteab<sup>3</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

<sup>2</sup>Colgate-Palmolive R & D, Inc., Avenue Du Parc Industriel, B-4041 Milmort, Belgium

<sup>3</sup>Colgate-Palmolive Co., Technology Center, 909 River Road, Piscataway, New Jersey 08854-5596

We demonstrate that the hydration repulsion between smooth charged surfaces can be attributed to the interplay of two effects which are not taken into account in the conventional DLVO theory. These are the

finite size of the counterions and the variable dielectric permittivity across the electric double layers. We involve these two effects in the theory by coupling the Poisson-Boltzmann equation with the Bikerman and Booth equations. The resulting nonlinear ordinary differential equation of second order is solved numerically. The theory is applied to interpret available experimental data for the dependence of the surface force on the distance measured by means of the surface force apparatus. Excellent agreement between theory and experiment is obtained with reasonable values of the two adjustable parameters: the area per surface charge and the counterion adsorption energy. It turns out that the contribution of the ionic excluded volume to the hydration force is several times greater than the contribution due to the dielectric saturation. The developed theoretical approach can find application for interpreting data about the interactions in aqueous thin films, colloidal dispersions and micellar surfactant solutions in the presence of electrolyte at ionic strengths above 1 mM.

### 308.C1 MEASURING ELECTROSTATIC DOUBLE-LAYER FORCES AT HIGH SURFACE POTENTIALS WITH THE ATOMIC FORCE MICROSCOPE

Roberto Raiteri<sup>1,2</sup>, Massimo Grattarola<sup>1</sup> and Hans-Jürgen Butt<sup>2</sup>

<sup>1</sup>DIBE, University of Genova, via Opera Pia 11A, 16145 Genova, Italy

<sup>2</sup>Institut für Physikalische Chemie, Universität Mainz, 55099 Mainz, Germany

The aim of this study was to measure interaction forces between surfaces with high electric potentials in aqueous electrolyte solutions. Therefore the force between a platinum or gold sample, which served as the working electrode, and a silicon nitride tip of an atomic force microscope was measured. Various potentials were applied between the sample and a reference electrode. Experimental results were compared to forces calculated with the Poisson-Boltzmann equation.

As predicted by theory the electrostatic double-layer force changed only in a narrow potential range of about 300 mV and saturated below and above this range. Within this range the repulsion grew with more negative sample potentials. This was expected since the tip was negatively charged at the high pH chosen. At strong negative sample potentials this saturation was not complete and the force continued to rise slightly when lowering the potential. Another surprising and yet unexplained observation was a weak long-range attraction at positive sample potentials. This attraction decayed with a decay-length of typically 50 nm.

In parallel the structure of gold (111) was imaged. We confirmed a ( $\sqrt{3} \times \sqrt{3}$ ,  $p > 10$ ) reconstruction at potentials below  $\approx -0.3 V_{SHE}$  and the normal (1 $\times$ 1) hexagonal packing above this potential. Above  $\approx +0.8 V_{SHE}$  the (1 $\times$ 1) structure disappeared and no crystalline packing was observed anymore.

### 309.C1 SURFACE FORCES IN FOAM FILMS FROM AMPHIPHILIC BLOCK COPOLYMERS

R. Sedev and D. Exerowa

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

The equilibrium thickness of microscopic foam films (radius  $\sim 100 \mu\text{m}$ ) obtained from aqueous solutions of different commercial poly(ethylene oxide) - poly(propylene oxide) - poly(ethylene oxide) triblock copolymers is experimentally determined. The influence of electrolyte (NaCl) concentration, pH, and pressure is examined. A pronounced influence of copolymer concentration below CMC is observed.

The dependence of the surface force on film thickness is monitored by the porous plate method. With this equilibrium technique the disjoining pressure is balanced with an outer pressure which can be suitably varied and measured.

The hydrophobic PPO block adsorb at the solution/air interface and the PEO tails form a brush layer. The thicker foam films are electrostatically stabilized. Charge creation can be attributed to preferential  $\text{OH}^-$  adsorption at solution/air interface. This electrostatic repulsion can be suppressed either by increasing the NaCl concentration or by lowering the pH of the solution (at constant ionic strength). In both cases a transition from electrostatic to steric stabilization occurs.

The thinnest foam films are sterically stabilized, but at lower pressure ( $\sim 500$  dyn/cm<sup>2</sup>) their thickness is larger than twice the brush layer thickness. While the total thickness  $h$  of these films strongly depends on the degree of polymerization  $N$ , its scaling structure is essentially the same: two brush layers of thickness  $h_1 \sim N$ , and an aqueous core of thickness  $h_2 \sim N^{3/5}$ . This scaling behavior suggests that the interbrush gap is filled out with swollen tails of the longest PEO chains as well as swollen coils from the bulk solution.

At higher pressure ( $\sim 5000$  dyn/cm<sup>2</sup> and up) the softer repulsion is overthrown and a brush-to-brush contact is realized. The disjoining pressure isotherm becomes much steeper and fairly agrees with predictions based on scaling arguments. Alternatively this steric repulsion can be seen as an elastic response of the compressed brushes. The higher pressure region can be characterized by a single modulus of elasticity.

### 310.C1

#### HYDRODYNAMIC INSTABILITIES OF COLLOID SYSTEMS AND NEW IDEA IN THE COLLOID AND INTERFACE SCIENCE

Viadimir Smorodin

*Inst. Tecnologia Quimica e Biologica, R. Quinta Grande, Apt. 127, P-2780, Oeiras, Portugal;  
Department of Chemistry, Lomonosov State University, Moscow 119899, Russia*

As it is known, a problem of (in)stability of colloid systems is a major and specific one of the colloid and interface science. And phenomena related with the coagulation (or aggregate) stability of colloids and films present the most practical interest. Studies of these phenomena stimulated an appearance of a new science on surface forces and its effects in thin polymolecular films [1]. The most important stages of development of fundamentals of this field were next:

- (1) Classical works of B. Derjaguin have been started in 30s years where he advanced a concept of the "disjoining" pressure;
- (2) a creation of the DLVO theory (by Derjaguin, Landau, Vervy and Overbeek). this theory described the force interactions in a system of lyophobic colloidal particles;
- (3) studies of stability of free and wetting films in research of Derjaguin and Titievskaya, de Vries, Vrij, Scheludko, Exerowa, Platikanov, Usiarov and many other scientists.

But in theoretical attempts to describe the fluctuation-hydrodynamic instability was a serious difficulty: how to take into account ion-electrostatic forces. First this problem was resolved in our work [2]. Later this task was generalized on a basis of the Navier-Stokes and the Boltzmann-Poisson equations for some the most interesting practical cases [3]. It permitted to generalize the Scheludko formula including the electrolyte effects (in a dependence of a critical film thickness on a wave length [4]).

- (4) Next important steps in understanding of the interactions of lyophobic colloids were made due to works of Derjaguin, Rabinovich, Tchuraev, Ruckenstein and others who developed hypothesis about quasi-cavitation phenomena [5].

Developing these idea in a work [2] it was proposed to include the hydrodynamic instability of boundary layer between interacting lyophobic particles in the theory. In the fact it expands a thermodynamic description of DLVO into the thermohydrodynamic one. On this basis it was understood a universal nature of such different phenomena as a microflotation [6] and hydrophobic interactions [7], as well as were advanced new "topologic" concepts of electrokinetic potential [2] and wetting films. A new theory of hydrophobic forces predicts a possibility to regulate "cell-cell" interactions using resonance thereby opening wide perspectives for modern biotechnology.

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### 311.C1 STRATIFICATION OF FOAM FILMS STABILIZED BY BOVINE SERUM ALBUMIN AND SODIUM DODECYL SULFATE: A QUANTITATIVE DESCRIPTION

K.D. Tachev<sup>1</sup>, J.K. Angarska<sup>2</sup>

<sup>1</sup>*Faculty of Biology, University of Shoumen, 9712 Shoumen, Bulgaria*

<sup>2</sup>*Faculty of Chemistry, University of Shoumen, 9712 Shoumen, Bulgaria*

Stepwise thinning (stratification) of foam films containing bovine serum albumine (BSA) and sodium dodecyl sulfate (SDS) has been studied. Films were obtained in a glass cell by the method of Scheludko and were observed by a metallographic microscope in reflected monochromatic light ( $\lambda=551\text{nm}$ ). The film thinning was studied by the micointerferometric method. The reflected light from a small part of the film surface was directed to a photomultiplier and the photocurrent was amplified and recorded by chart-recorder. From the output of the chart-recorder the data was collected by an ADC in a computer (with frequency of 100 MHz). The thickness of the film was calculated as a function of time. The obtained kinetic curve was processed by parts corresponding to the steps of the film thinning (each step ends with a transition to next metastable state of the film). Each part was interpolated to an empirical function and the velocity of the film thinning was obtained by numerical differentiation. The disjoining pressure was then determined as a function of the film thickness by the dynamic method. The obtained data was fitted to a theoretical curve of the disjoining pressure calculated by an expression proposed by Kralchevsky and Denkov (1993) describing the dependence of the oscillatory force on the film thickness. According to their results the stratification could be described by varying only the effective diameter of the particles in the solution (protein molecules) which reflects on the particle volume fraction.

Two concentrations of albumin were used in the present study ( $5 \times 10^{-5}$  M BSA and  $5 \times 10^{-4}$  M BSA) at a constant molar ratio of BSA:SDS=1:160 at which the most pronounced stratification was observed in our previously experiments. Films of the same concentrations of BSA and SDS containing 0.05 M NaCl were also studied.

The results of our experiments show that the proposed procedure is applicable to the study of stratifying films. A good correlation was achieved between the experimental data and the theoretical predictions for the disjoining pressure of stratifying film as a function of its thickness. The effective diameters of the BSA molecules obtained at the experimental conditions studied are acceptable as compared to the literature data. The role of NaCl on the protein solutions seems rather complicated. It acts as an electrolyte and suppresses the stratification. On the other side it affects the protein conformation changing the hydrodynamic shape of the macromolecules from ellipsoidal to spherical which is more favourable for stratification. Moreover, our results show that in the presence of NaCl the albumin molecules probably exist as dimmers. This supposition is confirmed by experimental data. The obtained effective diameter and the period of oscillating disjoining pressure assume that each transition during the stratification is a result of the expelling of a double layer from the film.

The model of oscillatory structural forces in the paper of Kralchevsky and Denkov (used in the presented study) deals with hard spheres. As known, the albumin molecules are ellipsoids (14x6 nm) and probably this is the reason for some complications observed when their semiempirical expression was used. In order to achieve correlation between the theoretical oscillating curve of the disjoining pressure and experimental data a different ratio between the effective particle diameter and the period of oscillations was applied instead of one predicted by the model.

### 312.C1 NORMAL AND SHEAR FORCES BETWEEN POLYMER-BRUSHES

Rafael Tadmor<sup>1</sup>, Joanna Janik<sup>1,2</sup>, Jacob Klein<sup>1</sup>, Lewis J. Fetters<sup>3</sup>

<sup>1</sup>*The Weizmann Institute of Science, Department of Materials and Interfaces, Rehovot, 76100 Israel*

<sup>2</sup>*on leave of absence from the Jagiellonian University of Cracow, Poland*

<sup>3</sup>*Exxon Research and Engineering Company, Clinton township, Annadale, New Jersey 08801, USA*

End functionalised poly(ethylene propylene) (PEP) was verified to form a solvated polymer brush in the good solvent cyclohexane. On this model system, normal and shear forces were investigated. Two opposing polymer brushes exhibit a very low friction coefficient when rubbed against each other. The friction coefficient remains low for high loads, in contrast to earlier studies, due to the low glass transition

temperature of the PEP. It is proposed that when the compressed PEP brushes slide at low shear velocities there is some inter penetration that results in weak entanglements between the opposing brush layers. As the shear amplitude is increased, the brush layers are forced to disentangle, and the friction drops, leaving weak interdigitation. This causes some drag force which is the main friction factor in this case. Our results provide a detailed picture of the relaxation of the brushes when the shear motion is stopped.

### 313.C1 THE STABILITY OF POLYSTYRENE LATEXES IN THE PRESENCE OF POLYMER-POLYMER COMPLEXES

**Tusupbaev N.K., Musabekov K.B.**

*Department of Colloid Chemistry, Faculty of Chemistry, Kazak State National University,  
Vinogradov Str. 95, 480012, Almaty, Republic of Kazakstan*

A synthetic polyelectrolytes and their associates with oppositely charged surfactants and polyelectrolytes are widely used to regulate the colloidal-chemical properties of disperse particles. However the mechanism of flocculation of interpolyelectrolyte complexes with respect to disperse particles is unclear. This communication deals with the study of the influence of polyethylenepolyamine (PEPA), polyethyleneimine (PEI), alkylated PEI (APEI), polydimethyldiallylammonium chloride (PDMDAC), polyacrylamide (PAAM) and their mixtures with polyacrylic (PAA) or polymethacrylic (PMAA) acids on the stability of monodisperse negative charged polystyrene latex particles. It has been shown that the increasing of the hydrophobicity of polymer chains leads to the decreasing of their stability effect. It is connected with the compactization of polymer chains leading to the formation of less amount of polymeric bridges. It has been established that the strong polyelectrolytes such as PEPA, PEI, PDMDAC and their complexes with PAA and PMAA flocculate the latex particles by means of neutralization mechanism, while more hydrophobic polyelectrolytes such as APEI, PAA and their complexes with PAA and PMAA act through the mechanism of bridge formation. One of the features of flocculation of latex particles by polyelectrolyte mixtures is the sequence of adding of components into the latex solution. The best effect is realized when to the latex solution the solution of cationic polyelectrolytes is firstly added. It is suggested that the association of PAA and PMAA with cationic polyelectrolytes can proceed not only on the surface of particles but also on the free part of macromolecules (tails) playing the role of bridges between several aggregated particles. As a result the hydrophobicity of particles increases and the density of aggregates becomes higher. All these factors lead to the increasing of the sedimentation velocity of the system. The mechanism of heteroflocculation takes place in the case of adding of interpolyelectrolyte complexes into the latex solution. Thus on the basis of spectrophotometric, viscometric and electrokinetic methods it is concluded that the destabilization of latex particles in the presence of cationic polyelectrolytes and their complexes with anionic ones proceeds either through the neutralization of particles charges or via the mechanism of formation of bridges and heteroflocculation.

### 314.C1 STRUCTURAL FORCES OF THE PARTICLE INTERACTION IN CONCENTRATED ELECTROLYTE SOLUTIONS

**O.Us'yarov. S. Blokhina**

*Agrophysical Institute, St. Petersburg, Russia.*

A radioisotope technique for studying the kinetics of the nondissolving volume with the use of  $^{36}\text{Cl}$  was developed. Suspensions of monoionic forms of montmorillonite in 1M solutions of chlorides of alkali and alkaline-earth metals (lithium, sodium, cesium and calcium) with a varying content of the solid phase were investigated. An increase in the content of chlorine ions in the dispersion medium, which is due to the appearance of liquid layers with a specific structure near the surface of clay particles and to structural forces of repulsion, is observed over the course of serial decades and may be approximated by an exponential function. The concentration of the solid phase significantly affects the value of the nondissolving volume: as the concentration increases, the effect is reduced until becomes nullified. The established regularities were explained on the basis of idea about the reversible aggregation of particles in suspensions. Using the experimental results the total forces of the interaction between particles are calculated. A method is

developed for determining, the parameters that characterized the range and magnitude of structural forces, as well as those for calculating the Hamaker constant as a function of the distance between the surfaces of microobjects. Possible errors on the accuracy of estimates is analysed. The effect of exchange cations on the interaction of particles is determined. It is shown, that ranges of the structural forces change in the same manner as the size of the hydrated exchange cations. The data on the minimum and maximum values at the potential curve of pairwise interaction are compared with the probability of a change in the interplanar distances in the lamellar structure of the clay mineral.

### 315.C1 DEPLETION FLOCCULATION: SOME RECENT OBSERVATIONS

B. Vincent<sup>1</sup>, P. Jenkins<sup>1</sup>, R. MacMillan<sup>1</sup> and A. Hemsley<sup>2</sup>

<sup>1</sup>*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 ITS, UK*

<sup>2</sup>*Dept. of Earth Sciences, University of Wales, Cardiff, CFI 3YE, UK*

1. Non-equilibrium effects in depletion interactions. It will be shown that for dispersions of hydrophobic silica particles in non-polar solvents, containing binary mixtures of polymers of different narrow M.W. fractions, that the critical (minimum) total polymer concentration ( $c_2^*$ ) for the onset of colloidal phase separation in the systems depends in an unexpected way on the composition of the polymer mixture. Indeed, it is demonstrated that ( $c_2^*$ ) depends on the order of mixing of the constituents. In further experiments with aqueous dispersions of hydrophilic silica particles, it is shown that, not only does ( $c_2^*$ ), on the addition of poly(acrylic acid), depend on the method of mixing, but so does the nature of the flocs obtained.

2. The role of depletion forces in a biological system will be described. Living and fossil megaspores produced by *Selaginella (lycopsida)* and its extinct ancestors form distinctive, iridescent exines. It will be shown that the iridescence is due to ordered arrays of bio-latex particles, and that these are induced by a depletion flocculation mechanism. Indeed, very similar systems can be produced "artificially" using polystyrene latex particles, on adding free, nonadsorbing polymer.

### 316.C1 POSSIBLE IMPLICATIONS OF HYDROPHOBIC SLIPPAGE ON THE DYNAMIC MEASUREMENTS OF HYDROPHOBIC FORCES

Olga I. Vinogradova

*Laboratory of Physical Chemistry of Modified Surfaces, Institute of Physical Chemistry,  
Russian Academy of Sciences, 31 Leninsky Prospect, 117915 Moscow, Russia*

It has earlier been shown that the capillary measurements may be interpreted in favour of hydrophobic slippage [1]. The possible implications of this phenomenon as regards the dynamic technique [2] for the hydrophobic attractive force measurements are discussed. We demonstrate that under experimental conditions the discernible deviations from the Reynolds theory due to slippage may occur [3]. Misuse of the Reynolds theory may lead to overestimation of hydrophobic attractive force. This apparent extra attraction depends critically on driving speed, and the types of surface interactions present in the system [4].

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### 317.C2 EFFECTS OF SHORT-CHAIN ALCOHOLS ON THE HYDRATION FORCES BETWEEN SILICA SURFACES

S. Vivek and R. -H. Yoon

*Center for Coal and Minerals Processing, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061*

It is difficult to predict the stability of colloidal silica suspensions using the DLVO theory. Yotsumoto and Yoon (1993) attributed the difficulty to the presence of hydration force, the evidence for which has been given from direct force measurements conducted by many investigators. The measured hydration forces are usually fitted using a double-exponential force law with its short-range decay lengths ( $D_1$ ) in the range of 0.05-0.6 nm and the long-range decay lengths ( $D_2$ ) in the range of 0.6-3 nm. Despite these experimental evidences, some investigators remain skeptical for the existence of hydration force, suggesting that non-DLVO repulsive forces measured in direct force measurements are due to surface roughness, the presence of silica gel or "hairs" of polysilicic acid, or due to the dielectric saturation effect.

In the present work, direct force measurements were conducted between silica surfaces in solutions of short-chain alcohols using an atomic force microscope (AFM). The value of  $D_2$  obtained in 10 and 20% by volume of ethanol solutions was 1.2 nm, which is substantially smaller than the value of 3.0 nm determined in Nanopure water. In a 15% methanol solution, however, the hydration force disappeared completely, allowing the force curve to be fitted perfectly to the DLVO theory. These findings are in agreement with our previous report (Yotsumoto *et al.*, 1994) that aqueous suspensions of silica can be destabilized by ethanol addition, which in turn has been attributed to the decrease in hydration force. The fact that short-chain alcohols cause a decrease in hydration force may be explained by the possibility that they adsorb on the silanol groups of the silica surface more strongly than the water molecules, thereby destabilizing the water structure in the vicinity. Apparently, methanol is more effective than ethanol in destabilizing the water structure, which may be related to the intoxication of humans by methanol intake. It is possible that short-chain alcohols, particularly methanol, displaces the water molecules bound to the polar heads of lipid membranes.

### 318.C1 INTERACTIONS BETWEEN COLLOIDAL PARTICLES

D.T. Wasan

*Department of Chemical Engineering, Illinois Institute of Technology, Chicago, IL 60616, USA*

The structure and stability of colloidal dispersions is highly dependent on the effective pair interactions (potential of the mean force) between colloidal particles. An overview is presented of the non-DLVO theory forces such as depletion and the surface-induced long-range oscillatory structural forces in colloidal dispersions. Particularly, the effective particle interactions in polydispersed colloidal dispersions are calculated using Monte Carlo simulations and the Ornstein-Zernike statistical mechanical theory. Effects of interparticle interaction on stability, aggregation and sedimentation in colloidal suspensions is illustrated with experimental data. New experimental evidence for the long-range attractions between the similarly charged colloidal spheres which are inconsistent with the accepted theory of colloidal interactions is presented.

### 319.C1 MONTE CARLO SIMULATION OF HAMAKER FORCES IN FREE LENNARD-JONES LIQUID FILMS

S.J. Winter, D.N. Theodorou, and C.J. Radke

*Chemical Engineering Department, University of California, Berkeley, CA 94720, USA*

Understanding the forces that control the stability of thin liquid films is important in the use of foams and emulsions. Disjoining pressure is a direct measurement of thin liquid film forces and their relationship to film thickness. For the first time, we employ Monte Carlo computer simulation to predict

disjoining pressure isotherms in the liquid films, based on the fundamental forces between molecules. A unique application of the Gibbs ensemble simulation is presented to study these thin films. By analogy to the experimental measurement of disjoining pressure, in which the film is in equilibrium with bulk liquid in the Plateau border, we implement a novel form of the constant-pressure Gibbs ensemble with two simulation boxes. One box contains the thin liquid film and the second contains the corresponding equilibrium bulk liquid. Because this composite ensemble allows the direct analysis of metastable phase coexistence, a thin film in equilibrium with its bulk liquid may be captured in a single simulation. Specifically, we set the difference in pressure between these two simulation regions (and hence, setting the disjoining pressure), leaving only the film thickness to be determined.

Intermolecular potential interactions are modelled using the Lennard-Jones equation. Attractive Hamaker forces result in the film. Preliminary results indicate that Hamaker's classic equation is obeyed for film thickness greater than several molecular diameters. Thus, Hamaker's constant is found from the slope of the curve of disjoining pressure versus one over film thickness cubed. Values of the Hamaker constants obtained from the simulation over a range of temperatures are in good agreement with those obtained from the traditional energetic summation procedure. From these initial results, we conclude that Monte Carlo Gibbs ensemble simulations appear very promising for the study of more realistic thin film systems.

## 320.C1

### SURFACE FORCES AND SURFACE COMPOSITIONS

V.V. Yaminsky

*Department of Applied Mathematics, Research School of Physical Sciences and Engineering,  
Institute of Advanced Studies, The Australian National University, Canberra, A.C.T. 0200, Australia*

Van der Waals and electric double layer forces of the classical DLVO, hydration, oscillatory solvation, hydrophobic and other non-DLVO forces, special surface forces that occur for soft matter, polymers and liquid crystals, as well as the capillary force itself obey the universal mass to energy relationship stated in the Gibbs adsorption equation. The derivative of the force with respect to the chemical potential (concentration, vapor pressure, *etc.*) of a component gives the change in its adsorption with distance between the surfaces. The accuracy of the adsorption result depends only on how accurately the chemical potential is controlled, the force is measured and the equilibrium is maintained in a surface force experiment. The thermodynamic analysis, rigorous in itself, is applicable to any reversible systems irrespective of their nature. The interlayer composition as a function of separation is the final result of a surface force measurement.

Among examples of practical applications we consider: (a) Different patterns of hydrophobic attraction in their relation to changes of water density and surfactant adsorption with separation, cavitation and capillary condensation. (b) A related issue: the equilibrium contact angle and its relation to the adsorption discontinuity at the three phase line. (c) DLVO and non-DLVO repulsive forces that arise from adsorption of ions, surfactants and polymers and self adsorption of the solvent. (d) Depletion and solvation forces that relate to oscillatory adsorption functions for the solute and the solvent. (e) Interaction in pure liquids in terms of vapor adsorption. (f) Adsorption and ion exchange effects in multicomponent media. (g) Long range structural effects and phase separation phenomena in confined liquid crystals. (h) Thermodynamic implications for Lifshitz theory of van der Waals forces; electric double layer and other theoretical models for adsorption profiles. The results are discussed in conjunction with classical application of the Gibbs equation in the areas of surface chemistry of surfactant solutions, stability of liquid films and electrocapillarity.

## 321.C2

### AGGREGATION OF SURFACTANTS ON SURFACES STUDIED BY SURFACE FORCES

Cissie Abraham and Mark Rutland

*School of Chemistry, University of Sydney, Sydney, Australia*

Recently it has been shown that the bilayer model of adsorption is completely inappropriate to describe the adsorption of typical single alkyl tail surfactants above the cmc, and that different adsorbed

structures are formed on different substrates by the same surfactant. It is not yet clear however, what characteristics of the surface influence the structure of the adsorbed aggregates

Measurements of forces between glass surfaces in solutions of the cationic surfactant CTAB (hexadecyltrimethyl ammonium bromide) at various pHs have been performed using the new MASIF instrument (Measurement and Analysis of Surface Interactions and Forces). Analysis of trends in apparent surface potential, the height of the force wall caused by adsorbed surfactant, and the distance of this force wall from contact of surfaces indicates that the structure of the adsorbed aggregate cannot be considered a classical bilayer, confirming recent measurements by other using atomic force microscopy and ellipsometry. However, as the surfactant concentration is gradually increased, the amount of adsorption to hydrophilic surfaces *below* the critical micelle concentration appears to determine the nature of the aggregate formed at concentrations *above* the cmc. Two different adsorption schemes are inferred from these measurements, depending on the degree of pre-cmc adsorption and both of which invoke the adsorption of sub-micellar aggregates. It is unlikely that AFM measurements would be able to distinguish between these two schemes.

### 322.C2 SPHINGOSINE-MEDIATED DNA TRANSFER THROUGH THE LIPID BILAYERS BY USING THE PATCH CLAMP METHOD

Nadejda Il. Christova and Iana Tsoneva

*Institute of Biophysics, Bulg. Acad. Sci., "Acad. G. Bonchev" str., bl. 21, Sofia - 1113, Bulgaria*

Lately the role of some lipids as sphingosine in mitogenic signal transmission via protein kinase C has been observed. Numerous recent studies have suggested the possible participation of cationic lipids in eucariotic transcription and replication process by some protein kinase C independent pathway. It was empirically suggested that sphingosine could exert its influence on cell growth via direct interactions with DNA. The biochemical and biophysical mechanism of complex formation and action of sphingosine-DNA systems have not known. Therefore further characterization of DNA-sphingosine interactions have needed.

In the recent communication by the method of patch clamp of bilayers formed from diphytanoyl lecithin and sphingosine in the presence of DNA are used for the investigation of the lipid-DNA interactions. We provide data that suggest DNA pass through the membrane by *long - lived metastable long linear as ellipse like defects*. The start of DNA-lipid interaction of the transfer of DNA through the bilayer is electrophoretic and depends on the polarity of the applied membrane voltage.

### 323.C2 FOAM FILMS STABILIZED WITH LYSOPHOSPHATIDYLCHOLINE: A COMPARISON OF MICROINTERFEROMETRIC AND FT-IR SPECTROSCOPY THICKNESS MEASUREMENTS

R. Cohen<sup>1</sup>, D. Exerowa<sup>1</sup>, T. Kolarov<sup>1</sup>, T. Yamanaka<sup>2</sup>, T. Tano<sup>3</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*Faculty of Education, Chiba University, Chiba 263, Japan*

<sup>3</sup>*Institute for Chemical research, Kyoto University, Uji, Kyoto-fu 611, Japan*

Previous studies<sup>1,2</sup> of foam films stabilized with the soluble phospholipid palmitoyllyso-phosphatidylcholine (lysoPC) have demonstrated the effect of  $\text{Ca}^{2+}$  ions binding by the phospholipid head group. Two different optical models have been used in these studies - the thin liquid film microinterferometric method and FT-IR spectroscopy. In both studies some additional treatment which relies on specific for the given technique assumptions for the film structure is needed to convert the measured data into real film properties. In the case of the microinterferometric method this is the three-layer sandwich model of the film structure. In the FT-IR spectroscopy the Lambert-Beer law with a molar absorption coefficient  $\epsilon = 150$  has been used to derive the aqueous core thickness from the film water content. In the present study thicknesses of common thin and black films determined by both optical methods are compared taking into consideration the assumed film structure models. It is demonstrated that the use of suitably selected optical parameters can lead to similar equilibrium film thicknesses. The obtained results are used in the analysis of the values and change of the potential of the diffuse electric layer  $\phi_0$  and charge density  $\sigma_0$  with  $\text{CaCl}_2$

concentration. The importance of the model assumptions necessary for the determination of parameters characterizing interaction forces in the film is demonstrated.

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## 324.C2 DRAINAGE BEHAVIOUR OF LIQUID FILMS ON MICA IN AQUEOUS SOLUTIONS OF GLICEROL AND GLICEROL-KCl

N.A. Debacher<sup>1</sup> and R.H. Ottewill<sup>2</sup>

<sup>1</sup>*Departamento de Química, Universidade Federal de Santa Catarina, Florianópolis, Brazil*

<sup>2</sup>*School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*

In this work the results of an investigation on the dependence of drainage time  $\Delta t$  of wetting films on mica surface using aqueous solutions of glycerol and glycerol with  $10^{-4}$  mol dm<sup>-3</sup> KCl are presented. The experimentally measured values are compared to those calculated using Reynolds equation:

$$\frac{d(1/h^2)}{dt} = \frac{4}{3\eta r_0^2} P_0 \quad (1)$$

where  $h$  is the thickness of the film,  $r_0$  is its radius, and  $\eta$  is the viscosity. The pressure  $P_0 = P + \pi$  is a sum of the capillary pressure  $P = 2\gamma_{LV}/R$  ( $\gamma_{LV}$  is the surface tension and  $R$  is the radius of the bubble, 0.2 cm) and the disjoining pressure  $\pi$ . In order to apply equation (1) to the dynamic method for the measurements of film thickness as a function of time, the film was ensured to be plane-parallel which was controlled visually.

The thickness of the film was determined as a function of time using the interferometric technique described in a previous work. The experiments were conducted with aqueous solutions of glycerol 4%, 10% and 20% and the same amount of glycerol with  $10^{-4}$  mol dm<sup>-3</sup> KCl. All measurements were performed at 25°C and the film radius was changed from  $0.34 \cdot 10^{-3}$  cm to  $2.50 \cdot 10^{-3}$  cm.

The drainage of the film was monitored from 204 nm to equilibrium and the plot of  $h$  versus time shows an increase in the time for reaching the equilibrium thickness as the glycerol concentration increased. However the equilibrium film thickness shows a decrease with the increase of glycerol concentration. From the slope of a plot of  $h^{-2}$  versus elapsed time when equation (1) is applied the experimental values of  $(4P_0/3\eta r_0^2)$  were obtained. These experimental values were compared with those calculated by applying equation (1). The experimental slope does not coincide with calculated values and the discrepancy between theory and experiment increases when  $10^{-4}$  mol dm<sup>-3</sup> KCl was added to the glycerol solution. The deviations in drainage behaviour from theoretical predictions may be explained on the basis that the main conditions for applicability of Reynolds equation are not fulfilled.

The equilibrium film thickness shows a small variation with the increase in film radius and glycerol concentration. This variation is even smaller when an aqueous solution of glycerol with  $10^{-4}$  mol dm<sup>-3</sup> KCl is used although the drainage time increases linearly with the viscosity of the bulk solution.

## 325.C2 pH-INDUCED TRANSITION FROM ELECTROSTATIC TO STERIC STABILIZATION IN FOAM FILMS FROM ABA BLOCK COPOLYMERS

D. Exerowa, R. Ivanova, R. Sedev

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

The effect of pH on the equilibrium thickness of microscopic foam films from amphiphilic block copolymers of ethylene oxide (EO) and propylene oxide (PO) is investigated. Experiments are carried out with two nonionic copolymers: EO<sub>27</sub>PO<sub>39</sub>EO<sub>27</sub> (Synperonic P85) and EO<sub>122</sub>PO<sub>56</sub>EO<sub>122</sub> (Synperonic F108). A strong effect of pH (pH = 2 - 6) on the film thickness,  $h_w$ , (at constant ionic strength) is found in both cases. The film thickness decreases with decreasing pH. At a particular pH value a transition to black films ( $h_w = 15$  nm) for P85 and to dark gray films ( $h_w = 40$  nm) for F108 is observed. The parameter  $pH_{cr}$  [1] marks the transition to black films in the case of P85,  $pH_{cr} = 3.8$ . In the case of F108 the parameter  $pH_{cr,sl}$  is introduced

to distinguish the transition to thicker, sterically stabilized films,  $pH_{cr,st} = 3.2$ . Further decreasing of pH has no detectable influence. This behavior is analogous to that of low-molecular nonionic surfactants described earlier: electrostatic interaction in foam films from nonionic surfactants arises from preferential  $OH^-$  adsorption at the liquid/air interface [2]. Above the critical values of pH films are electrostatically stabilized. Electrostatic disjoining pressure can be suppressed either by increasing the total electrolyte concentration (i.e. shrinking the diffuse double layer) [3] or by increasing the concentration of the  $OH^-$  counterions, i.e. lowering pH. While foam films from nonionic surfactants rupture at lower pH, foam films from block copolymers do not - a transition from electrostatic to steric stabilization occurs [4]. This transition is characterized by the parameter  $pH_{cr,st}$ .

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## 326.C2 INFLUENCE OF SOLID STATE SURFACE ON MOLECULAR & STATISTIC PROPERTIES OF WATER.

Gloskovskaya N.<sup>1</sup> V., Heinzinger K.<sup>2</sup>, Ilyin V. V.<sup>1</sup>

<sup>1</sup>*Bogolyubov Institute for Theoretical Physics, Kiev, Ukraine*

<sup>2</sup>*Max-Planck-Institute für Chemie (Otto.-Hahn-Institute), Mainz, Germany*

Investigations of surface phenomena in water systems are undertaken to solve a number of fundamental and applied problems. Theoretical study of these phenomena with analytic methods is, as a rule, difficult to realize. Therefore, computer experiment methods are used to obtain necessary information.

In our calculations with the help of computer experiment methods (Monte-Carlo and molecular dynamics methods) we used several models of water, where water molecule was treated as rigid system, as molecule with internal degrees of freedom, as flexible molecule which can dissociate. We considered thin films and layers, confined with ideal impenetrable surface, surface with active centers, metal surfaces, magnesium oxide surface.

Energetic, structural, dynamical and spectroscopic characteristics of water systems near the boundary were investigated. Effect of orientational ordering of water molecules near the surface was analyzed and its stability to external influences was studied. Criteria of surface hydrophilicity were considered on microscopic level. A number of results on anisotropy of transport characteristics in the region near the surface and on the charge of spectroscopic characteristics in comparison with the bulk ones were obtained. The hydration process of magnesium oxide clusters surface was investigated and the dependency of spectral characteristics on their size was analysed. Cooperative effects contribution in water systems interacting with the surface was studied.

## 327.C2 INFLUENCE OF THE ELECTRIC CHARGE DENSITY ON THE ELASTIC CONSTANTS OF AMPHIPHILIC FILMS, DETERMINED BY SCATTERING EXPERIMENTS

M. Gradzielski<sup>1</sup>, B. Farago<sup>2</sup>, H. Hoffmann<sup>1</sup>

<sup>1</sup>*Lehrstuhl für Physikalische Chemie I, Universität Bayreuth, D - 95440 Bayreuth, Germany*

<sup>2</sup>*Institut Laue-Langevin, B.P. 156, F-38042 Grenoble Cedex 9, France*

The properties of surfactant systems can be described in terms of the bending elasticity of the amphiphilic film. This elasticity is characterized by two moduli, the mean bending modulus  $k$  and the Gaussian modulus  $k'$ . A particularly simple system for that type of description are microemulsion droplets since, due to their typically low interfacial tensions, the bending energy should be the leading term in the free energy of the system.

Oil-in-water microemulsions of an originally unchanged system made up from a zwitterionic surfactant, hexanol as cosurfactant, and a hydrocarbon can become successively charged by the substitution of the nonionic surfactant by a cationic surfactant. In this system spherical microemulsion droplets are present, where the size is controlled by the amount of cosurfactant (and accordingly the amount of hydrocarbon that is solubilized) as shown by scattering experiments.

In this investigation the amount of ionic surfactant is varied while keeping the size of the droplets constant, or for a given degree of ionic substitution the ionic strength of the solution is varied. For these microemulsions the macroscopic interfacial tensions were measured and the structure of the corresponding droplets was determined by means of small-angle neutron scattering (SANS). From the SANS experiments in shell contrast the polydispersity index  $p$  of the droplets can be deduced with good precision. Via the obtained polydispersity index  $p$  the bending moduli of the surfactant film can be calculated and the same can be done independently from the interfacial tension values  $\gamma$ .

From this experiment the sum of the bending constants can be deduced as a function of the charge density of the droplet system (or of the ionic strength). The charging process of the interface should lead to a stiffening of the amphiphilic film and the corresponding changes in the experimental parameters (interfacial tension and polydispersity index) are observed. The obtained changes as a function of charge density and ionic strength are compared to theoretical expressions derived from electrostatic theories of the curved interface.

## 328.C2

### STABILITY OF EVAPORATING THIN LIQUID FILMS IN THE PRESENCE OF SURFACTANT

**T.D. Gurkov and K.D. Danov**

*Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry,  
University of Sofia, James Bourchier Avenue 1, Sofia 1126, Bulgaria*

We study the fluctuation dynamics in evaporating liquid films, in the presence of dissolved surfactant. The film covers a flat solid substrate which is subjected to heating. The liquid-vapor interface is regarded as a two-dimensional continuum characterised by specific adsorption, interfacial viscosity, and surface tension. These quantities depend on the surfactant subsurface concentration and the temperature. In the case of thin films, at small Reynolds and large Peclet numbers, we apply the lubrication approximation model. The effect of the intermolecular forces, that is, the disjoining pressure, is taken into account. There are contributions of the van der Waals, electrostatic, steric, and oscillatory structural interactions (the latter are operative when micellar aggregates exist in the film). The hydrodynamic equations are cast into dimension-less form using specific groups of physical parameters. Linear stability analysis (for small perturbations) is performed by calculating the critical wavelength at which the fluctuations grow up to rupture for minimum time [1]. Numerical solution of the time evolution equation was implemented, providing information for the critical thickness of film rupture. Computations in the frame of the non-linear theory were carried out as well. The influence of the interfacial mass loss due to evaporation, the intermolecular forces, the Marangoni effects arising from thermal and concentration gradients, and the interfacial viscous friction upon the critical film thickness is discussed.

The problem for the linear stability of two immiscible liquid layers on a substrate was considered in a similar manner. Important stabilising or destabilising effects, connected with positive or negative Hamaker constants of the van der Waals forces, were discovered. In the particular case of water-on-hexane films we found that at small temperature differences (below 1°C) the stability is substantially influenced by the surfactant concentration. When the latter rises one observes a transition from fully mobile to immobile oil/water interface. Simultaneously, the critical thickness of rupture of the hexane film declines.

I. K.D. Danov, N. Alleborn, H. Raschiller, F. Durst (1997) *Physics of Fluids* (submitted).

### 329.C2 OSCILLATORY STRUCTURAL FORCES AND STRATIFICATION OF THIN LIQUID FILMS: THEORY AND EXPERIMENT WITH EMULSION FILMS

P. A. Kralchevsky, N. D. Denkov, T. D. Gurkov and K. Marinova

*Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics Faculty of Chemistry, University of Sofia, 1 James Bourchier Avenue, Sofia 1126, Bulgaria*

Oscillatory structural forces appear in two cases: (i) in thin films of pure solvent between two smooth *solid* surfaces; (ii) in thin liquid films containing colloidal particles (including macromolecules and surfactant micelles). In the second case, the structural forces give rise to the phenomenon stratification of liquid films. At higher particle concentrations the structural forces stabilize the liquid films and colloids. At lower particle concentrations the structural forces degenerate into the *depletion attraction*, which is found to destabilize various dispersions.

To quantify the oscillatory structural force we obtained a relatively simple formula, which describes its dependence on both film thickness and particle volume fraction [1]. This expression is successfully tested against the predictions of integral equations, computer simulations and experimental data for the step-wise transitions in the thickness of stratifying films.

In addition, we obtained experimental data for both thickness and contact angle of stratifying emulsion films formed from micellar solutions of the *ionic* surfactant *sodium nonylphenol polyoxyethylene-25 sulfate*. The theoretical and the experimental values of the contact angle, are found to coincide in the framework of the experimental accuracy [2]. The *metastable* states of the film correspond to the *minima* of  $f$  vs  $h$  curve, where  $f$  is the excess free energy due to the surface forces and  $h$  is the film thickness. The depth of the minima increases with the decrease of the electrolyte concentration because of the increase of the micelle effective volume fraction, which includes the Debye counterion atmospheres. As a result, the contact angle increases with the decrease of electrolyte concentration. This tendency is exactly the opposite to that in the absence of micelles (surfactant concentrations around and below CMC), when oscillatory structural forces are missing. For the investigated systems the contribution of the oscillatory force to the contact angle turns out to be much greater than the contributions of the electrostatic and van der Waals forces.

1. P.A. Kralchevsky and N.D. Denkov, "Analytical Expression for the Oscillatory Structural Surface Force." *Chem. Phys. Letters* 240 (1995) 385 - 392.

2. K.G. Marinova, T.D. Gurkov, T.D. Dimitrova, et al. "Role of the Oscillatory Structural Forces for the Interactions in Thin Emulsion Films Containing Micelles" *Langmuir* (1996) - submitted.

### 330.C2 BLACK FOAM FILMS STABILISED BY INSOLUBLE AMPHIPHILE MONOLAYERS

R. Krustev<sup>1</sup>, H.J. Müller<sup>2</sup>, D. Platikanov<sup>1</sup>, L. Richter<sup>2</sup>, G. Kretzschmar<sup>2</sup>

<sup>1</sup>*Department of Physical Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

<sup>2</sup>*Max-Planck Institute for Colloids and Interfaces, 12489 Berlin, Germany*

The experimental device for investigation of microscopic foam films stabilised by monolayers of insoluble amphiphile surfactants has been improved. The film has been obtained by carefully pressing of an air bubble on the orifice of a capillary tube against the lower side of the water surface in the Langmuir trough covered by insoluble monolayer. A microscopic circular film is formed on the top of the bubble in this condition. The film is observed in reflected light by microscope. The two dimensional surface pressure ( $\pi$ ) of the monolayer and the pressure in the bubble have been measured. The monolayers have been prepared from dimyristoyl phosphocholine (DMPC) and dipalmitoyl phosphatidylcholine (DPPC) spread on 0.15M NaCl aqueous solution at 25°C. The probability for black film formation and mean lifetime of the films with constant radius have been studied. The results show that films can be obtained only if the surfactant monolayer is spread on both film's surfaces. In all cases if there is a monolayer on the upper surface only the films rupture immediately after formation. The black films can be observed in the region of the  $\pi(A)$  isotherm where liquid expanded state occurs. The probability for film formation increases with decreasing area per molecule ( $A$ ) in the monolayer. The mean films' lifetime increases with decreasing area per

molecule as well. The films become indefinitely stable in the region of liquid condensed phase. Films prepared from DMPC monolayers are less stable than these from DPPC at the same area per molecule.

### 331.C2

#### PERMEATION OF GAS THROUGH NEWTON BLACK FILMS AT DIFFERENT CHAIN LENGTH OF THE SURFACTANT

**R. Krustev, D. Platikanov, A. Stankova, and M. Nedyalkov**

*Department of Physical Chemistry, University of Sofia, Bulgaria*

The gas permeability of Newton black foam films stabilised by four alkyltrimethylammonium chloride homologues - dodecyl-, tetradecyl-, hexadecyl- and octadecyltrimethylammonium chloride (DoDTACl, TDTACl, HDTACl and ODTACl) has been measured. Sodium chloride with constant concentration 0.5M was added in the aqueous surfactant solutions. The experimental results demonstrate well-pronounced dependence of the gas permeability coefficient  $K$ , cm/s on the surfactant alkyl chain length.  $K$  decreases with increasing chain length. The temperature dependence of  $K$  for the same films has been studied as well.

The results are discussed on the basis of the nucleation theory of fluctuation formation of clusters of molecular vacancies (holes) in the foam bilayers. The gas permeation occurs both through holes and through hole-free part of the film (background permeability  $K_0$ ) according to the theory. The experimental data have been used for better understanding the mechanism of gas permeation through the hole-free area of the bilayer Newton black film. Two main theories for gas permeation through monolayers on liquid surfaces are used. According to the *simple diffusion theory* the hole-free part of the bilayer is considered as a homogeneous phase. Hence,  $K_0$  should depend reciprocally on the film thickness, i.e. on the surfactant chain length. According to the *energy-barrier theory* the gas molecules pass through the spaces between the surfactant molecules in the bilayer. In this case  $K_0$  should depend exponentially on the number of methylene groups in the surfactant alkyl chain: Our results are in favour of the energy-barrier mechanism of permeation through the hole-free film.

### 332.C2

#### GAS PERMEABILITY THROUGH BLACK FOAM FILMS FROM SODIUM DODECYL SULPHATE

**R. Krustev, D. Platikanov, M. Nedyalkov, A. Stankova**

*Department of Physical Chemistry, University of Sofia, Bulgaria*

Two experimental methods for measurement of the permeability coefficient  $K$ , cm/s for the permeation of air through black foam films have been developed. They allow investigation of the gas permeability of black films in a wide range of thermodynamic conditions.

Series of measurements of  $K$  of foam films from sodium dodecyl sulphate plus sodium chloride or lithium chloride aqueous solutions at constant surfactant concentration and temperature have been performed. Experimental results about the dependencies of  $K$  on NaCl or LiCl concentration are reported. A jump wise decrease of permeability  $K$  at the transition from common black film (CBF) to Newton black film (NBF) has been found. The  $K$ -values of the thinnest NBF are 2-3 times lower than those of the essentially thicker CBF. The results show that the gas permeation through black foam films is mainly determined by the properties of the surfactant layers: two monolayers in the CBF or a bilayer in the case of NBF.

The dependencies of  $K$  of NBF on surfactant concentration  $C$  at four temperatures have been studied. The gas permeability strongly depends on  $C$  at low concentrations but it remains constant at higher  $C$ . The permeability increases with increasing temperature. The experimental data are discussed on the basis of the nucleation theory of fluctuation formation of holes in amphiphile bilayers. Clusters of molecular vacancies (holes) exist in the bilayers according to the theory. Gas permeation occurs simultaneous through the hole-free film area (background permeability) and through the holes. The results are in favour of an essential contribution of hole-mediated permeability at lower surfactant concentrations and higher temperatures.



## 333.C2

## OSCILLATING PHENOMENA IN THIN LIQUID FILMS

Ph. Letocart<sup>1</sup>, H. J. Schulze<sup>1</sup>, B. Radoev<sup>2</sup><sup>1</sup>Max-Planck-Institute for Colloid and Interface Science, Research Group  
at the Freiberg University for Mining and Technology, Freiberg/Saxony, Germany<sup>2</sup>Dept. of Physical Chemistry, University of Sofia, Bulgaria

Many papers have shown the crucial importance of critical surface waves on the stability of Thin Liquid Films (TLFs) [i.e. 1,2,3]. In these analyses it was shown that the rupture of both asymmetric (i.e. water films on quartz) and symmetric films (i.e. soap films) is due to growing of thermal surface fluctuations at critical thickness of film.

In order to investigate this aspect of stability an experimental setup was build to produce acoustically external excited surface waves on circular wetting TLFs of diameter about 300  $\mu\text{m}$  (water on quartz). A microinterferometric technique was used to determine the dynamic thickness of the film at two different places (diameter of measuring point: 1  $\mu\text{m}$ ), in order to measure the phase shift of a free running wave inside the film.

In accordance with the theory that establishes highly damped waves, the oscillations vanish totally in the middle of the film. Thus reflection in the centre can be neglected and the hypothesis of free running wave is acceptable for close measuring points (practical distance: 5  $\mu\text{m}$ ).

By mean of Fast Fourier Transform of the two thickness signals, analysis of such artificial waves delivers directly an information on the dispersion relation, which describes the dependence of the wave number to the exciting frequency. A comparison with the theoretical approach of the dispersion relation of TLFs gives the first derivative relative to the film thickness of the disjoining pressure  $\Pi$ .

A first comparison between experiment and theory shows higher gradients of  $\Pi$  values than the theoretically predicted ones.

1. Donners W. A. B., Vrij, A. (1978), Coll. Polym. Sci. 252; 982
2. Radoev, B., Scheludko, A. D., Manev, E, J. Coll. Int. Sci. 95; 1
3. Sharma, A., Ruckenstein, E., J. Coll. Int. Sci. 119; 1

## 334.C2

## RUPTURE OF LIPID MEMBRANES

Marcus Lindemann and Mathias Winterhalter

Dept. of Biophysical Chemistry, Biozentrum, Universität Basel,  
CH-4056 Basel, Switzerland

We applied short electric field pulses across lipid bilayers. One pulse charges the membrane and give raise to electric forces. Above a critical threshold voltage rupture of the membrane is induced and a fast discharge of the membrane across the defect is observed. An analysis of the time course of the voltage gives information on the energy barrier of the membrane against rupture and allows conclusion on the kinetics of the defect widening. Our setup allows to follow the kinetics from the  $ns$  to  $s$  range. We observed that in planar lipid membranes held under tension the defect spreads very fast with about 0.1-0.3 m/s. Creating a polymer network by polymerizing action onto the lipid membrane causes a qualitative change in the rupture kinetics. The rupture process is now determined by the membrane viscosity and not anymore by the inertia of the lipid [1]. We show evidences for membrane fluctuations and the resealing of ion conducting defects.

1. M. Lindemann, M. Steinmetz and M. Winterhalter, *Prog. Colloid Polymer, Sci.* (1997).

**335.C2 PROPERTIES OF THIN LIQUID FILMS STABILISED BY PROTEINS****K.G. Marinova<sup>1</sup>, T.D. Gurkov<sup>1</sup>, R.P. Borwankar<sup>2</sup> and B. Cambell<sup>2</sup>**<sup>1</sup>*Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, University of Sofia,  
Faculty of Chemistry, James Bourchier Avenue 1, Sofia 1126, Bulgaria*<sup>2</sup>*Kraft General Foods, Inc., Technology Center, 801 Waukegan Road,  
Glenview, Illinois 60025, USA*

We investigated thin aqueous films, stabilised by Bovine Serum Albumin (BSA) and  $\beta$ -casein. The film behaviour is time-dependent. The contact angle increases with ageing, and exhibits a pronounced hysteresis. With BSA one observes slow reversible aggregation on the surface (but not in the bulk), the protein lumps are gradually squashed by the capillary pressure as the film thins. Our findings can be explained by slow surface denaturation, accompanied with developing attraction and partial entanglement of the BSA molecules, which ultimately leads to firm sticking of the two interfaces of the film [1]. Marked difference in the surface mobility is observed with foam and emulsion films stabilised by BSA. Lenses, containing protein aggregates and liquid, when surrounded by area which has reached the black film stage, remain entrapped in foam films for more than an hour but are squeezed out for minutes in emulsion films. The hydrophobisation of the protein molecules in contact with oil may be responsible for this behaviour. The electrostatic interactions are found to be important: without salt the films stay thick, whereas in the presence of 0.15 M NaCl one obtains Newton black films whose contact angle depends upon the molecular charge.

With  $\beta$ -casein ageing effects in films are noticed only at the isoelectric point. This protein strongly aggregates in the bulk, but the lumps are readily flattened on the film interfaces. Addition of  $\text{Ca}^{2+}$  ions leads to decrease of the film thickness, depending on the concentration. Above a threshold concentration of  $\sim 12$  mM  $\text{Ca}^{2+}$ , a drastic increase of the contact angle and the energy of adhesion is observed. A cross-binding of the two opposing film surfaces occurs. The effects can be explained with adsorption of  $\text{Ca}^{2+}$  on some particular aminoacid residues of casein, which leads to congestion of the adsorbed protein layer and cross-linking. Thus, important specific factors may affect the stability of emulsions with proteins.

1. K.G. Marinova et al., *Colloids Surfaces* (1996) in press.

**336.C2 MODEL STUDY ON EMULSION SYSTEMS  
WITH HIGH INTERFACIAL MOBILITY****Elena Mileva, Ljubomir Nikolov***Institute of Physical Chemistry, Bulgarian Academy of Sciences,  
"Acad. G.Bonchev" Str., bl. 11, Sofia 1113, Bulgaria*

Most of the basic characteristics of the dynamic properties of the emulsion systems may be adequately analyzed by the study of the following model situation: two droplets creepingly approach each other along their common axis at small separations. Based on the existence of different geometrical and dynamic scaling parameters in the problem of close-distance interactions, the Stokes equations may be simplified to several sets of asymptotic equations. The new point here is that the interfacial mobility is immanently introduced in the scaling procedure. The advantage of our approach is that it searches the asymptotics in the hydrodynamic equations, which are then solved exactly. That is in contrast to the usually applied procedure of searching the asymptotics in the general expressions for the extensive quantities, like the drag force, where the real dependence on the tangential mobility and its combined effect with the small-gap restrictions may be concealed. The major result of our study is the correct formulation and the mathematical solving of the equations for the thin layer between the droplets. The case of low-viscosity fluid particles is analysed. It is shown that the lubrication theory equations cannot model correctly the hydrodynamics of the layer. Simple expressions for the first-order velocity and pressure fields are obtained. The results are used to construct expressions for the drag force and the coalescence speed in the surfactant-free case.

### 337.C2 THE BOUNDARY LAYER AND STABILITY OF THE HYDROPHILIC DISPERSIONS

V.N. Moraru, F.D. Ovcharenko, D.V. Moraru

*Institute of Biocolloidal Chemistry, National Academy of Sciences of Ukraine,  
42 Vernadsky blvd, 252142 Kyiv, Ukraine*

The results of experiments on different factors influence on the structure and extent of the hydration boundary layers (HBL) upon the surface of oxidized synthetic diamond (OSD) and oxidized graphite (OG), with the subsequent registration of the age in the thickness of the hydrodynamically immobile HBL by the electrokinetic method and obtaining an independent information concerning the surface charge ( $\sigma$ ), the  $\zeta$ -potential and the sol stability in the wide pH and indifferent electrolyte concentration interval are presented.

The influence of the following four factors: hydrophilization (by increasing the oxidation degree) of the graphite and diamond surface, preliminary thermal treatment of micropowder in the inert gas flow, the temperature dependences of the electrophoresis and stability of the OSD and OG dispersions, introduction of the non-ionic compounds, for example, saccharose, promoting the HBL structure destruction, on the HBL thickness was studied in order to test the method correctness and reliability.

It is established that during the action of each of these factors on the HBL the sign of the  $\zeta$ -potential changes strictly correlates with the direction of the slip boundary shift that serves as an additional argument in favour of the conception laid in the method base.

On the base of the obtained dependences of  $\zeta=f(C_{KCl})$  at  $\sigma(pH)=const$  and  $\zeta=f(\sigma_s)$  at constant ionic strength using the known equations of the diffuse DEL theory the quantitative estimation of the thickness of the hydrodynamically immobile HBL on the OSD and OG surface which varies within the limits  $h = 1.0 - 3.0$  nm was carried out. The obtained  $h$  values for the OSD and OG using different approaches keep within the mentioned limits and on an average meet the HBL thickness in 5 - 7 molecular water layers.

These results quantitatively agree with the experimental data on the stability of the dispersions under investigation as well as with the calculations of the potential curves of the pair particle interaction in the OSD and OG dispersions according to the generalized DLVO theory with the structural forces account.

### 338.C2 INVESTIGATION OF FOAM FILMS AT HIGH DISJOINING PRESSURE

H. J. Müller

*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Berlin-Adlershof, Germany.*

The investigation of single foam films is able to deliver information on the forces of interaction between the film surfaces and on the facts limiting the stability of foams. Several methods have been used for studying model soap films. Films for example have been drawn from the film forming solution in a vertical frame or formed in a small horizontal ring. If there is any repulsive disjoining pressure in the film it thins out until the inner disjoining pressure equals the applied outer pressure. In this way it is possible to measure the dependence of disjoining pressure on film thickness. The maximum accessible disjoining pressure amounts to some thousand Pa for films in vertical frames and around 50 Pa in the ring.

Higher values have been reached with the so-called porous plate method. In this experimental setup a pressure of at maximum  $10^6$  Pa can be applied on the surfaces of the foam film, while the interior of the film is connected with a bulk solution outside under normal pressure via the pores of a porous glass plate.

This communication describes the development and application of an isopiestic method for film formation following an idea of Clunie [Clunie et al., *Nature* 216 (1967), 1203]. This method makes accessibly the measurement of the disjoining pressure in a single foam film until  $10^8$  to  $10^9$  Pa. The foam film is formed from a very small volume of the film forming solution in a closed container. However, the water vapour pressure in the container is adjusted to a given value by two different methods:

(i) A salt solution with a volume large compared with that of the film forming solution was also situated in the container.

(ii) A special compartment was inserted in the container with a temperature lower as in the rest of the container by a certain adjustable difference- $\Delta T$ . This condenser trap was isolated sufficiently against transport of heat, but open for exchange of vapour.

After a time for equilibration the vapour pressure near the film is equal that above the salt solution or in the condenser trap. The disjoining pressure accessible in the film by this isopiestic method is given by the relation:

$$\Pi = -(RT/v) \ln(p/p_0)$$

( $\Pi$  : disjoining pressure,  $R$ : gas constant,  $T$ : temperature in Kelvin,  $v$ : molar volume of water,  $p$ : equilibrium vapour pressure in the cell given by the vapour pressure of the salt solution or in the condenser trap,  $p_0$ : vapour pressure above a volume phase of the film forming solution).

In this work the isopiestic method for film formation was applied on films from solutions of the surfactants sodium dodecyl sulphate (SDS) and heptaoxyethylene dodecyl ether ( $C_{12}E_7$ ). The dependence of the repulsive disjoining pressure was measured until around 14 atmospheres and a transition to the very thin (bilayer) Newton black film above this value was observed. Films from SDS and  $C_{12}E_7$  are stable until very high values of the pressure. The equilibration of films from SDS solutions with concentrated salt solutions gave rise to crystal-like arrays in the film.

This method allows to check theories of the interaction forces between interfaces in foam films in a more extended range. The measured repulsive forces are much larger than predicted from the DLVO theory of the electrical double layer repulsion. The results were discussed, therefore, in relation to a new theory of film interaction enhanced by changing adsorption [Müller, H. J. submitted to J. Phys.Chem.] and to contributions of ion-ion correlation and hard core interaction.

### 339.C2

#### DRAINAGE OF MICROSCOPIC FOAM FILMS FROM BSA AND ITS ENHANCEMENT WITH PLURONIC L62

Zs. Németh<sup>1</sup>, R. Sedev<sup>2</sup>, R. Ivanova<sup>2</sup>, T. Kolarov<sup>2</sup>, and D. Exerowa<sup>2</sup>

<sup>1</sup>Physical Chemistry Department, Technical University of Budapest, H-1521 Budapest, Hungary

<sup>2</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Recently Németh et al. [1,2] studied the good antifoaming properties of Pluronic L62 with respect to foams from Bovine Serum Albumin (BSA). Here we study the thinning of microscopic films from BSA, L62 and their mixture.

The foam film drainage has been carried out in a Scheludko-Exerowa cell and the film thickness has been monitored interferometrically. All experiments were done with fresh aqueous solutions in 0.1 M NaCl (25 °C).

**BSA** Films from BSA (4 g/L) exhibit a complex rheological behavior. The drainage as observed in reflected monochromatic light is irregular and quite slow. The film thickness,  $h_w$ , varies from point to point along the film surface and finally a black film is formed ( $h_w = 25$  nm).

**L62** Films from L62 ( $4 \times 10^{-5}$  mol/L) drain very regularly as already observed with other Pluronics [3]. The thinning of thicker films follows Reynolds equation:

$$\frac{dh_w^{-2}}{dt} = \frac{4P_c}{3\eta r^2}$$

where  $\eta$  is the bulk viscosity,  $r$  the film radius (160 - 240  $\mu$ m) and  $P_c$  (= 640 dyn/cm<sup>2</sup>) the capillary pressure (sucking the liquid out of the film).

Below 100 nm film drainage is faster than predicted by this equation. This acceleration can be reasonably attributed to van-der-Waals attraction (Hamaker constant  $(7-14) \times 10^{-13}$  erg). Finally the film ruptures. Most probably the PEO chains of L62 ( $EO_9PO_{30}EO_9$ ) are too short to create significant steric stabilization.

**BSA + L62** Films from a mixture of BSA + L62 drain more like the pure L62 films within the first minute or so. The smaller L62 molecules adsorb quickly at the liquid/air interface (as detected with surface tension measurements) and create similar conditions for drainage as in the L62 case. The effective viscosity is higher and can be correlated to the BSA molecular size. After several minutes the adsorption of BSA comes into play and thinning becomes irregular. The interference fringes look more like the pure BSA case and the dynamic method cannot be applied.

The investigation of the drainage of these films shed some light on the mechanism of the homogeneous antifoaming.

2. Zs. Németh, Gy. Rácz, and K. Koczó (1997) Proc. 7th Conf. Coll. Chem., Budapest.
3. R. Sedev, T. Kolarov, and D. Exerowa (1995) Colloid Polym. Sci. 273, 906.

### 340.C2 RUPTURE OF COMMON BLACK FILMS: EXPERIMENTAL STUDY

A. Nikolova and D. Exerowa

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

The dependence of the mean lifetime  $\tau$  of microscopic horizontal common black foam films from sodium dodecyl sulphate on the surfactant concentration  $C$  is studied at various electrolyte concentrations  $C_{el}$  by the thin liquid film microinterferometric technique. These data are used for determination of the surfactant concentration  $C_\tau$  at which the common black films have a constant mean lifetime. Thus the parameter  $C_\tau$  is proposed as a new characteristic of the black foam film stability at different electrolyte concentrations. The dependence  $C_\tau(C_{el})$  is obtained within the range 0.1-0.5 mol.dm<sup>-3</sup> NaCl. The results for the stability of the common black films are compared with the ones for the foam bilayers (Newton Black Films). It is shown that the stability of the black films  $C_\tau$  is constant above 0.2 mol.dm<sup>-3</sup> NaCl. This fact grounds the hypothesis that the thin common black films (thickness below 8.8 nm) rupture by hole nucleation mechanism described in the theory of Kashchiev and Exerowa for the bilayer stability.

### 341.C2 PHASE STATES OF FOAM BILAYERS

A. Nikolova and D. Exerowa

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

For a long time it was thought that the foam bilayers (Newton black films) have a constant thickness which does not change with the electrolyte concentration, temperature and pressure. We have shown that this is not true as far as the foam bilayers can exist at different phase states. The phase states of foam bilayers from phospholipids and lipid-protein mixtures were studied by the thin liquid film microinterferometric technique. Occurrence of chain-melting phase transition was detected for foam bilayers from individual phospholipids (dimyristoylphosphatidylcholine, DMPC, and dipalmitoylphosphatidylcholine, DPPC) by two independent experimental parameters - the critical concentration  $C_C$  for formation of foam bilayer and the foam bilayer thickness. The critical concentration for formation of foam bilayer was obtained from the dependence of the probability for observation of foam bilayer in common foam film on the bulk concentration of amphiphile molecules. The data for  $C_C$  are discussed in terms of the hole-nucleation theory of Kashchiev and Exerowa for the stability of bilayers. The binding energy of a phospholipid molecule in the foam bilayer and the line tension of the nucleus hole are calculated for the liquid crystalline and gel state of the bilayers. Coincidence of the temperature and enthalpy of this transition is found for the foam bilayers from DMPC and the dispersions from which they were formed. This approach was applied also for the analysis of the phase state of foam bilayers from natural lipid-protein mixtures. It is shown that these bilayers do not undergo phase transitions and are in the liquid crystalline state within the temperature range studied. Occurrence of orientation and conformational phase transitions in lipid and lipid-polymer foam bilayers is detected also.

### 342.C2 FOAM BILAYERS FROM DIPALMITOYLPHOSPHATIDYLCHOLINE: FORMATION AND PHASE STATES

A. Nikolova<sup>1</sup>, R. Koynova<sup>2</sup>, B. Tenchov<sup>2</sup> and D. Exerowa<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

Microscopic horizontal foam bilayers (Newton black films) from dipalmitoylphosphatidylcholine (DPPC) have been studied by the thin liquid film microinterferometric technique. The foam bilayers were

formed from DPPC dispersions in water and in a water/ethanol (52.5:47.5, vol/vol) mixture in the presence of  $0.15 \text{ mol.dm}^{-3}$  NaCl. The high ethanol concentration strongly facilitates their formation. The experimentally determined bilayer thickness and the critical bulk concentration  $C_c$  of DPPC required for the formation of a stable microscopic foam bilayer from the water/ethanol mixture were measured in the range 35–45 °C. Both parameters indicate co-operative changes in the state of the foam bilayers. These changes take place at the temperatures of the bulk chain-melting phase transitions, as determined by differential scanning calorimetry (DSC) for both aqueous and water/ethanol DPPC dispersions. The critical DPPC concentration  $C_c$  for the water/ethanol dispersions changes between 55 and  $140 \mu\text{g cm}^{-3}$  in the range 35 – 45 °C. However, measurements by DSC show that decreasing the lipid concentration to  $2.5 \mu\text{g cm}^{-3}$  in both water and water/ ethanol mixtures does not affect the enthalpy, temperature and width of the bulk phase transition of DPPC. This is an indication that the DPPC molecules in the foam bilayer are in equilibrium with the ones in the vesicles. A concentration-temperature phase diagram of DPPC foam bilayers that defines the regions of gaseous (ruptured), gel and liquid crystalline foam bilayers has been constructed.

### 343.C2

#### FOAM FILMS FROM CATIONIC SURFACTANTS: SURFACE FORCES AND STABILITY

A. Nikolova, R. Yankov, D. Exerowa and D. Kashchiev

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

Foam films stabilised by the cationic surfactants dodecyltrimethylammonium acetate (DTAOAc) and hexadecyltrimethylammonium acetate (HTAOAc) were studied in a broad range of electrolyte concentrations by the thin liquid film pressure balance technique and thin liquid film microinterferometric technique. Long-range and short-range surface forces are determined. The transition between them occurs at  $0.6 \text{ mol.dm}^{-3}$  NaAc and at  $1 \text{ mol.dm}^{-3}$  NaAc for the HTAOAc and DTAOAc films respectively. Disjoining pressure/film thickness,  $\Pi(h)$ , isotherms were measured at different electrolyte concentrations. It is shown that at the low electrolyte contents the interaction forces in the foam films studied follow the DLVO theory. The diffuse layer potential and the surface charge density are estimated from the  $\Pi(h)$  isotherms. It was found that the thickness of the foam bilayers (Newton black films) was independent on the applied pressure similarly to the foam bilayers from numerous ionic and nonionic surfactants studied in our earlier works. Experimental dependence of the mean lifetime of the foam bilayers on the surfactant concentration was measured. These data were analysed by the hole-nucleation theory of Kashchiev and Exerowa for the bilayer rupture. The following characteristics of the foam bilayers were calculated: the supersaturation, the line tension of the nucleus hole, the number of single vacancies in the nucleus hole, the work for formation of nucleus hole and the binding energy of an amphiphile molecule in the foam bilayer.

### 344.C2 ELECTROSTATIC INTERACTION IN FOAM FILMS FROM NONIONIC SURFACTANTS: THE INFLUENCE OF CHAIN LENGTH

R. Sedev and D. Exerowa

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

A simplified picture of the electrostatic interaction in foam films from nonionic substances is presented and the influence of the hydrophilic chain length is discussed.

The equivalent film thickness,  $h_w$ , of foam films from miscellaneous surfactants is experimentally determined as function of electrolyte concentration,  $C_{EL}$ , at constant temperature, surfactant concentration, pressure ( $\sim 500 \text{ dyn/cm}^2$ ) and pH ( $\sim 5.5$ ). The influence of  $C_{EL}$  is of primary importance at lower ionic strength and therefore electrostatic interaction is present. At sufficiently high electrolyte concentration a plateau value,  $h_{w\infty}$ , is reached:

$$h_w = h_{w\infty} \text{ when } C_{EL} > C_{EL,CR}$$

Below  $C_{EL,CR}$  electrostatic repulsion dominates. If so, the film thickness,  $h_w$ , should decrease as the distance,  $d$ , between the two planes of the diffuse double layers

$$h_w \cong d \cong l/\kappa \sim \frac{l}{\sqrt{C_{EL}}}$$

A good linear dependence between  $h_w$  and  $C_{EL}^{-1/2}$  is observed all cases thus confirming the electrostatic nature of the interaction. Via linear extrapolation a value,  $h_{w0}$ , can be determined:

$$h_w \xrightarrow{C_{EL}^{-1/2} \rightarrow 0} h_{w0}$$

For low molecular weight surfactants both values coincide confirming that the  $\phi_0$ -plane is located at the inner edge of the adsorption layer. For surfactants with longer hydrophilic chain (including PEO-PPO-PEO block copolymers) a discrepancy is found. The difference is a nonlinear function of the molecular weight, i.e. chain length of the surfactant.

### 345.C2 MOLECULAR AND STRUCTURAL COMPONENTS OF DISJOINING PRESSURE IN WETTING AND ADSORPTION FILMS OF UNPOLAR LIQUIDS ON POLAR SURFACES

Semashko O.<sup>1</sup>, Us'yarov O.<sup>1</sup>, Stavinsky Y.<sup>2</sup>, Zorin Z.<sup>3</sup>

<sup>1</sup>Agrophysical Institute, St. -Petersburg, Russia

<sup>2</sup>Institute of Agrophysics, Lublin, Poland

<sup>3</sup>Institute of Physical Chemistry, Moscow, Russia

The dependence of disjoining pressure  $\Pi$  as a function thickness  $h$  of asymmetrical liquid layers of unpolar substances on polar surfaces is investigated. The wetting films of tetradekane on mica and glass and adsorption films of nitrogen, methane, hexane and benzene on graphitized black are studied. It is shown, that for all systems under consideration are not agreement with calculations based on the Lifshitz theory of van der Waals forces. That deviation can be caused by action structural component of disjoining pressure, arising due to the different orientation of molecules near surfaces a solid - liquid and liquid - gas. The magnitude and radius of structural forces were defined. It was discovered, that structural component determines significant the thickness of wetting and adsorption films of unpolar liquids on the polar substrates. Representing isotherm  $\Pi(h)$  as a sum of molecular and structural components it is possible to give the satisfactory explanation for observable regularity on qualitative and quantitative levels. Parameters of structural forces as thin and rather thick asymmetrical films are determined and compared with the well known experimental data. The analysis of received results has allowed to conclude that structural component of disjoining pressure as the function of film thickness can be submitted as the sum of two exponential dependences and each of them answers correlation distances about 0.1 and 1 nm, correspondingly.

### 346.C2 DRAINAGE OF A THIN LIQUID FILM TRAVERSING A SINUSOIDAL PORE

Gurmeet Singh, George J. Hirasaki, and Clarence A. Miller

Department of Chemical Engineering, Rice University 6100 South Main Street,  
Houston, Texas 77005-1892 USA

Numerical simulation of behavior of a thin liquid film as it traverses a sinusoidal pore has been performed. Effects of surface elasticity and viscosity and of disjoining pressure have been included. The thickness of a film with nearly immobile surfaces remains greater than its equilibrium value as its radius increases in moving from a pore throat to a pore body. Indeed, when the film moves rapidly through the pore, the relation between its thickness and its speed is similar to that found by Bretherton for the thickness of the liquid film surrounding a long bubble traveling along a cylindrical capillary tube. In contrast, the thickness of a film with mobile surfaces drops below its equilibrium value during passage from pore throat to pore body. Under appropriate circumstances, such a film can become unstable and break. These results are relevant for foam flow through porous media, which is of interest in connection with certain processes for enhanced oil recovery and remediation of ground water aquifers contaminated by organic liquids.

### 347.C2 CRITICAL THICKNESS OF THE GAP BETWEEN TWO DROPS AND THE MECHANISM OF COALESCENCE IN EMULSIONS

Simeon D. Stoyanov and Krassimir D. Danov

*Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry,  
University of Sofia, James Bourchier Avenue 1, Sofia 1126, Bulgaria*

New theory of the critical thickness of the film between two emulsion droplets in the presence of surfactant was developed. During the process of film drainage the corrugation of the film surfaces induces small fluctuations in the velocity, pressure, and surfactant concentration. The non-perturbed state was calculated by taking into account the real shape of the film surfaces, including the peripheral menisci (the Plateau border). The frequently used simplification that the real film is plane-parallel turns out to be inappropriate for the stability analysis; in fact, the meniscus zone appears to be important. In the frame of the lubrication approximation the linear problem of the film stability analysis reduces to a system of stiff differential equation for the amplitudes. The coefficients of the system depend on the average velocity of film thinning and on the derivative of disjoining pressure. By formal minimization of the film rupture time as a function of the wavelength one derives an explicit expression for the critical film thickness. The theory was applied for the interpretation of available experimental data for the critical thickness of aniline films stabilized by dodecanol. The observed increase of the critical thickness with the increase of the film radius and with the decrease of the surfactant concentration is consonant with the theoretical predictions. The influence of the Gibbs elasticity, interfacial viscosity and diffusivity on the film rupture time was demonstrated. The concentration range of stability of the primary emulsion films was calculated by applying the linear fluctuation analysis to films stabilized with ionic surfactant. The influence of the surface potential and electrolyte concentration on the magnitude of the fluctuation increment was calculated. In the framework of the developed dynamic theory we examined also the relative importance of the steric, van der Waals and electrostatic surface forces for the film stability.

Next we applied the results for the stability of a separate emulsion film to describe the kinetics of coalescence in batch emulsions. We investigated the relation between the hydrodynamic theory of film stability and the empirical Bancroft rule.

### 348.C2 INVESTIGATION OF DMPC FOAM FILMS

J.L. Toca-Herrera<sup>1</sup>, H.J. Müller<sup>1</sup> and D. Exerowa<sup>2</sup>

<sup>1</sup>*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Berlin-Adlershof, Germany*

<sup>2</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

Foam films can be formed from suspensions of the lipid DMPC in water and mixtures of water and ethanol. On convenient conditions such foam films thin out to a bilayer. Such foam bilayer films represent a suitable model method for the investigation of the behavior and the structure of two dimensional phases of lipids. The results can be compared with investigations of monolayers. In the case of the bilayer foam film the structure may be influenced by the interaction of the two monolayers in the film.

We have determined the conditions for the preparation of such films and the influence of the content of ethanol and salt on the film thickness. Phase transitions in the bilayer film and its structure were investigated by interferometric thickness measurements, analysis of stability of the bilayer, ellipsometry and fluorescence microscopy.



### 349.C2 EFFECTS OF CATIONS ON INTERACTION FREE ENERGIES AND CORE THICKNESSES IN BLACK FOAM FILMS STABILIZED BY LYSOPHOSPHATIDYL-ETHANOLAMINE. COMPARATIVE STUDY WITH LYSOPHOSPHATIDYLCHOLINE FILMS

T. Yamanaka<sup>1</sup>, Y. Tanaka<sup>1</sup>, T. Tano<sup>1</sup> and R. Cohen<sup>2</sup>

<sup>1</sup>Laboratory of Chemistry, Faculty of Education, Chiba University, Inage-ku, Chiba 263, Japan,

<sup>2</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

A thin liquid film is treated as a liquid layer bound by two geometrical surfaces, where the distance between the surfaces is so small that interaction occurs. Interaction free energy in Newton black film (NBF) of macroscopic, vertical foam film can be obtained by measurement of the difference ( $\Delta F$ ) in tensions between the black film and the bulk surface by use of a technique based on the principle of the Wilhelmy plate method for surface-tension determination and an electro microbalance.

In the present study, the  $\Delta F$ s have been measured on the black foam films stabilized by lauroyllysophosphatidylethanolamine (lysoPE) and palmitoyllysophosphatidylcholine (lysoPC) as a function of salt concentration of monovalent ( $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ), divalent ( $\text{Ca}^{2+}$ ) and trivalent ( $\text{La}^{3+}$ ) cations used as chlorides. In addition, the temperature dependence of  $\Delta F$  has been measured on the black films formed from aqueous solutions of lysoPE and lysoPC and also in the presence of NaCl and  $\text{CaCl}_2$ . Further, the core thicknesses ( $d_2$ ) have been separately measured on the black films stabilized with lysoPE as a function of  $\text{CaCl}_2$  and NaCl concentrations. The values of  $d_2$  were determined from measurement of the absorbance at absorption band for liquid water assigned to the fundamental OH-stretching frequency at  $3400\text{ cm}^{-1}$ , by use of the FT-IR spectrometer.

In a previous paper, we measured the  $\Delta F$ s for the black films formed from aqueous dispersion of dimyristoylphosphatidylcholine (DMPC) as well as from solution of lysoPC as a function of salt concentration of monovalent ( $\text{Na}^+$  and  $\text{K}^+$ ), divalent ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$ ) and trivalent ( $\text{Eu}^{3+}$ ) cations used as chlorides [*J. Colloid Interface Sci.* 1982, 88, 458]. Further, we measured the  $d_2$  for the equilibrium film of lysoPC in the presence of  $\text{CaCl}_2$  and NaCl [*Langmuir* 1994, 10, 1871]. Each lipid forms the NBF from salt-free solution:  $\Delta F = -0.24\text{ mJ/m}^2$  and  $d_2 = 1.2\text{ nm}$  for lysoPE, and  $\Delta F = -0.021\text{ mJ/m}^2$  and  $d_2 = 2.5\text{ nm}$  for lysoPC. The effects of added cations on  $\Delta F$  and  $d_2$  are similar in both lipids. The addition of divalent, trivalent cations and  $\text{Li}^+$  cause the thickness-transition from NBF to common black film or silver-equilibrium film and the increase of  $\Delta F$  at a definite salt concentration depending upon the nature of salts and lipids. These phenomena arise from an appearance of double-layer repulsive forces due to the ion binding in the film. It is noteworthy that the transition concentration of each salt for lyso PE is higher than that for the lysoPC.

### 350.C2 MULTILAYER SYSTEM OF NANOPARTICLES WITH A BILAYER MEMBRANE TEMPLATE

Tetsu Yonezawa and Toyoki Kunitake

Department of Chemical Science and Technology, Faculty of Engineering, Kyushu University, Fukuoka 812-81, Japan

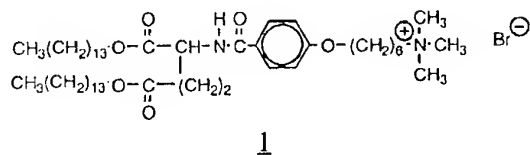
Nanoscope inorganic colloids and clusters - nanoparticles - have been known for a long time. They produced renewed interests these days from the view point of novel properties. In particular, gold nanoparticles are most widely investigated for the purpose of chemical, biological, medical, and physical studies. Metal and semiconductor nanoparticles may be useful as functional units in nano-electronic devices based on the quantum electrical effect.

Sodium 3-mercaptopropionate (MPA)-stabilized gold nanoparticles in water were prepared by a modified citrate reduction system. We inject MPA in concurrent with the addition of citrate ion (reluctant) in a boiling solution of tetrachloroauric(III) acid ( $\text{HAuCl}_4$ ). Only the simultaneous injection of reluctant and stabilizer could produce stable dispersions of MPA- stabilized nanoparticles. Separate addition did not give stable dispersions. The obtained dispersions remained stable for several weeks without aggregation or precipitation.

Nanoparticles thus obtained are extremely uniform. The particle size of gold particles could be controlled simply by stabilizer/gold ratios. Citrate reduction without stabilizer gives gold nanoparticles with

the diameter of ca. 20 nm (our result: 19 nm). In the presence of MPA, sizes of gold nanoparticles became much smaller. The smallest size obtained in this study was ca. 2.3 nm.

Lipid bilayer membranes have been widely investigated as a powerful technology in supramolecular chemistry. Recently, two dimensional inorganic clusters templated by bilayer membranes have been studied extensively. Two dimensional array of gold nanoparticles is interesting from a point of view of SERS substrates and quantum dot array system. However, ordered multilayer system of condensed gold nanoparticles has not been reported yet.



We could obtain two dimensional arrays of MPA-stabilized gold nanoparticles with a bilayer membrane template. Self-supporting red or golden films were obtained by casting mixed solution of an ammonium amphiphile **1** and MPA-stabilized gold nanoparticles on a substrate. Gold

nanoparticles are incorporated into the interlayers of the amphiphile **1**. Detail characterization of the film is now in progress.

### 351.C3 ANALYSIS OF PHYSICAL DESTABILISATION MECHANISMS OF CONCENTRATED DISPERSIONS BY THE TURBISCAN MA 1000

Gérard Meunier

*FORMULACTION, Toulouse, France*

Emulsion instability is often the result of a conjunction of two different physical processes :

- 1 - A particle size increase (droplets or aggregates) due to coalescence or flocculation phenomena.
- 2 - A particle migration within the samples giving rise to creaming or sedimentation.

Creaming or sedimentation are often considered as benign reversible phenomena while coalescence spells disaster for the formulator. It is, thus, of the utmost importance to detect very early on these phenomena in order to shorten the aging tests and to improve the formulations.

The TURBISCAN MA 1000 is a vertical scanner which analyzes light transmission and back scattering. It is able to detect minute concentration and particle size variations in the sample earlier than the operator's naked eye specially with concentrated suspensions.

We demonstrate, in this paper, the TURBISCAN potential to perform kinetic stability studies with various concentrated dispersions (emulsions, suspensions, foams). In addition, we show that the presence, the absence and the position of the isobestic point (scanning curves intersecting point) provide information on the nature of the physical process involved in the destabilisation of the mixtures and on their kinetic of appearance.

### 352.C3 SiO<sub>2</sub> AEROGEL PARTICLES DISSOLUTION: KINETICS AND LIGHT SCATTERING

A.G. Okunev, A.F. Daniluk, and Yu.I. Aristov

*Boriskov Institute of Catalysis, pr. Lavrentieva 5, Novosibirsk 630090, Russia*

Aggregation and gelation of SiO<sub>2</sub> colloid particles in solutions are being intensively studied for last decades and a structures of gels formed have been postulated. In contrary, the backward processes of gel dissolution and disintegration still need to be carefully investigated, especially with in situ experimental techniques. The process of gels partial dissolution may be of interest both from practical (modification of gel properties, nanoparticles and nanocluster preparation) and scientific points of view, because a mechanism of gels disintegration provides an opportunity to compare theoretical and computational models with actual experiments. In the present work, the kinetics of silica dissolution in NaOH aqueous solution is measured. The experiments have been performed under kinetically controlled isothermal conditions. Base-catalyzed aerogels prepared by one step technique [1] and commercial silica gel of Davisil-60 type (Aldrich Chemical) are used for the experiments. Aerogel samples are partially dissolved, and the kinetics of the process is registered by measuring the total concentration of both monosilicic acid and its polymer forms in solution (by the method of silicomolybdic acid formation [2]). Data analysis shows that the aerogel dissolution

proceeds via disintegration of the macrostructure at conversion degrees about 30%. Moreover, due to the uniformity of interparticle bonds of the studied aerogels this process may exhibit a threshold behavior typical for percolation structures. Complementary experiments on in situ UV scattering in the range 240 - 300 nm have also shown unusual dependencies of the solution optical density and light scattering on time. Two well separated peaks are observed in the case of aerogel dissolution while kinetic curves of silica gel exhibit one peak only which is correlated in time with the second peak in aerogel kinetic curves. The first peak in aerogel kinetic curves may be identified as corresponding to the aerogel destruction at percolation threshold. The nature of the second peak has not been quite understood yet. In our opinion, the interplay of kinetic and diffusion rate constants may cause the process of secondary aggregation of aerogel primary particles while their size decreases. Preliminary TEM data also indicate that the second peak may be caused by the process of backward aggregation. This study was supported in part by the Russian Basic Research Foundation (Grant N 97-03-32471).

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### 353.C3

#### CHARGE INTERACTIONS IN SEMI-CONCENTRATED CERAMIC OXIDE SUSPENSIONS

**J.B. Rosenholm, S. Durand-Vidal and M. Kosmulski**

*Department of Physical Chemistry, Abo Akademi University, 20500 Abo, Finland*

The interaction between ceramic oxide particles have been investigated in dilute and semi-concentrated suspensions as a function of pH and the ionic strength using acoustophoresis. Since the acoustophoresis may contain significant errors the influence of the particle size and the background electrolyte on the response signal was evaluated.

It was found that an erroneous large signal was found in very dilute suspensions as well as for large particles. Moreover, the signal increased if the pH was successively varied by the addition of NaOH and HCl.

However in the semi-concentrated regime with particles smaller than ca. 2  $\mu\text{m}$  the acoustophoresis seems to give accurate information of the charge interactions between the particles in the suspension.

### 354.D1 SPHERE-TO-ROD TRANSITION IN THE SHAPE OF MICELLES OF ETHOXYLATED ALKYL SULFATES IN THE PRESENCE OF MULTIVALENT COUNTERIONS

R.G. Alargova<sup>1</sup>, V. Ivanova<sup>1</sup>, G. Broze<sup>2</sup> and A. Mehreteab<sup>3</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

<sup>2</sup>Colgate-Palmolive Research and Development, Inc. Avenue Du Parc Industriel, B-4041 Milmort (Herstal), Belgium

<sup>3</sup>Colgate-Palmolive Co., Technology Center, 909 River Road, Piscataway, NJ 08854-5596, USA

The properties of ionic micelles of sodium dioxyethylene-sulfate (SDP-2S) in the presence of multivalent ions are investigated by means of light scattering methods. It is shown that divalent, and especially trivalent counterions, may lead to dramatic change in the micellar size and shape even at very low ionic strengths. This effect is particularly pronounced for trivalent counterions as  $\text{Al}^{3+}$ . The cylindrical shape of the large micelles has been established by measuring the angular dependence of the scattered light. The solubilization capacity of SDP-2S is shown also to be dependent on the presence of multivalent ions. It is found that at constant surfactant concentration cylindrical micelles are more effective in the solubilization process than spherical ones [1]. This observation is of practical importance because it is directly related to the cleaning action of given surfactant composition.

We present also experimental data showing that surface tension,  $\sigma$ , of SDP-2S solutions undergoes a substantial change in a vicinity of the transition from sphere to cylinder in the micelle shape (the 2nd CMC). In the experiments we fixed the ionic strength of the added electrolyte, but varied the molar fractions of NaCl and  $\text{AlCl}_3$ . We established that the observed variation of  $\sigma$  in a vicinity of the 2nd CMC can be attributed to two competitive effects: (i) competition between  $\text{Na}^+$  and  $\text{Al}^{3+}$  counterions for the adsorption in the subsurface Stern layer, and (ii) competition between the solution surface and the surfaces of the micelles to adsorb the  $\text{Al}^{3+}$  counterions. We develop a theoretical model which allows to calculate the true bulk (background) concentrations of  $\text{Na}^+$  and  $\text{Al}^{3+}$  ions, and the variation of  $\sigma$  in the vicinity of the 2nd CMC. Good agreement between theory and experiment is achieved. The results show that the transition from sphere to cylinder in the micelle shape (the 2nd CMC) can be detected by surface tension measurement.

I. R. Alargova, J. Petkov, D. Petsev, I.B. Ivanov, G. Broze, A. Mehreteab, *Langmuir*, 1995, 11, 1530.

### 355.D1 SHAPE TRANSFORMATIONS OF GIANT UNILAMELLAR VESICLES UPON INTERDIGITATED GEL PHASE FORMATION

M. I. Angelova, R. Mutafchieva, B. Tenchov

*Institute of Biophysics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Shape transformations of dimyristoylphosphatidylcholine (DMPC) vesicles accompanying induced by ethanol formation of an interdigitated phase were investigated by phase contrast microscopy. Giant unilamellar vesicles (50-80  $\mu\text{m}$  in diameter) were prepared by the liposome electroformation method (1,2). The bilayer interdigitation was induced by using ethanol concentration of 2.6 M. The kinetics of the vesicle shape changes were followed by an image-processing video system. A general property of this process, independent of the initial phase to which ethanol was added, was the formation of foldings. These foldings are consequence of the excess area of the interdigitated phase and the low water permeability of the membranes. Another general property of the various transitions to the interdigitated phase, starting from the phases  $\text{L}_\alpha$ ,  $\text{P}\beta'$  or  $\text{L}\beta'$ , is the increased contact area of adjacent adhering vesicles, presumably due to a higher membrane/water surface tension of the interdigitated bilayers. The degree of folding upon formation of the interdigitated phase depends on both the initial phase state and the duration of incubation in the latter before addition of ethanol. The highest degree of folding was observed for initial  $\text{L}\beta'$  phase after short incubation, and the lowest - for initial  $\text{P}\beta'$  phase after 18 hours incubation before addition of ethanol. These foldings were much better expressed for vesicles incubated in  $\text{P}\beta'$  phase for 30 min compared to vesicles incubated in

$P\beta'$  for several hours. We consider this a manifestation of the slow formation of the  $P\beta'$  phase. The budding of the vesicles is an event that precedes folding in the transitions from  $P\beta'$  or  $L\alpha$  to the interdigitated phase.

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### 356.D1 SURFACTANT SELF-ASSEMBLY AT AN IONIC CRYSTAL SURFACE INVESTIGATED USING AFM

D. Bokern and W. A. Ducker

*Chemistry Department, University of Otago, Dunedin, New Zealand*

The molecular organisation of quarternary ammonium surfactant on the barium sulfate (001) surface in aqueous solution has been studied by atomic force microscopy (AFM). In dilute solution below the critical micelle concentration (cmc) the surfactant molecules are preferentially adsorbed at defect surface sites, forming tube-like surface aggregates. At surfactant concentrations around the cmc the formation of a self-assembled monolayer/bilayer was observed, which suggests a stronger total interfacial force between surfactant and surface than reported for other substrates (e.g. graphite and mica).

### 357.D1 CLUSTER MODEL OF THE ORDERING PROCESSES IN AQUEOUS SOLUTIONS

I. V. Brovchenko<sup>1</sup>, A. V. Oleinikova<sup>2</sup>

<sup>1</sup>*Institute of Physics, Kiev, Ukraine*

<sup>2</sup>*Kiev Taras Shevchenko University, Ukraine*

The ordering processes in the aqueous solution of organic molecules we considered in view of the peculiarities of hydrogen bonding between water and hydrophilic groups of solute molecules. Two main kinds of the water clusters, bonded with the hydrophilic group of the solute molecule, are found: water-like and organic-like. In water-like cluster single water molecule is bonded with the hydrophilic group of the solute molecule via one strong H-bond and another three H-bonds between this water molecule and surrounding water are possible. Cooperative effects in the H-bond's network of water lead to the creation of the water-like cluster, containing dozens water molecules. If water molecule is bonded with the hydrophilic group of the solute molecule via two H-bonds, only two H-bonds with surrounding water are possible. As a result only a few water are in the corresponding organic-like cluster.

The water-like clusters provide better embedding of organic molecules in H-bond's network of water in comparison with organic-like ones, besides the water-like clusters have strong tendency to self-assembly. At some "critical" concentration water-like clusters merge all together in the water-like phase and it results in the macroscopic ordering of the mixture. In the simplest case the mixture separates on the water-rich and organic-rich phases, which consist of the water-like clusters and organic-like clusters, respectively. The thermoreversible gelation and formation of micelles are considered as uncompleted phase separation. Merging of the water-like clusters provides flexible bonds between the hydrophilic groups at appropriate distances and leads to the formation of gel. Extraction of the water-rich phase, consisting of the water-like clusters, promotes formation of micelles, which in one's turn consist of the organic molecules, bonded with organic-like water clusters.

The organic-like clusters have lower energies and less possible configurations in comparison with the water-like ones. Together with the general decreasing of the number of H-bonds with increasing temperature it results in the specific temperature dependence of the concentration of the water-like clusters with maximum at some temperature. The intersections of this dome-like temperature dependence with the line of the "critical" concentration of the water-like clusters correspond to the temperatures of the phase transitions.

The temperature dependence of the concentration of the water-like clusters were calculated for the aqueous solutions of pyridines, tetrahydrofuran and polyethylene glycol using the method of atom-atom

potentials. The changes of the absolute values of the lower and upper critical consolute temperatures with deuteration of water or solute molecules, addition of electrolytic impurities, embedding of the alkyl substituents in solute molecule were reproduced quantitatively in the framework of the proposed cluster model.

### 358.D1 THE STRUCTURE AND PHASE BEHAVIOUR OF SOME LONG CHAIN CERIUM(III) CARBOXYLATES

Hugh D. Burrows, Eduardo Marques and Maria da Graça Miguel

*Departamento de Quimica, Universidade de Coimbra, 3049 Coimbra, Portugal*

The long chain carboxylates (soaps) of polyvalent metal ions are important both at the technical level as catalysts, driers, polymer stabilizers, etc, and at the research level as models for more complex lipid systems. Many of these applications depend on the phase behaviour of these compounds, where one or more mesophases are frequently observed on heating the pure compounds [1]. Because of their catalytic activity, and their valuable spectroscopic and magnetic properties, it is anticipated that the long chain carboxylates of trivalent lanthanide ions will be of considerable interest. However, surprisingly little has been reported on these compounds. A few studies have been reported on synthesis, thermal degradation, magnetic, spectral properties and solution behaviour [see, for example, 2,3]. However there is a clear need for more systematic study.

We have synthesized and characterized the even chain length carboxylates  $(\text{Ce}(\text{O}_2\text{C}(\text{CH}_2)_n\text{CH}_3)_3)$ , for  $n$  between 6 and 16. Thermogravimetric analysis shows the presence of coordinated water for the short chain homologues synthesized by metathesis. However, the longer chain soaps only contain adsorbed water, and this can be removed by heating. These differences are explained by the competition between the coordination requirements of the metal ion and the packing of the hydrocarbon chains. X-ray diffraction and infrared spectral measurements show that the solid phase of the carboxylates have a lamellar, layered structure, with planes of the cerium(III) ions coordinated to the carboxylate groups.

The phase behaviour of these compounds has been studied by differential scanning calorimetry (DSC) and optical observations using a polarising microscope. One or more mesophases are observed between the solid and isotropic liquid phases on heating to 70-100 °C. Both the temperatures of this first phase transition, and the overall enthalpy of melting of the carboxylates increase with increasing chain length. The textures observed on the polarizing microscope clearly show the anisotropic nature of these mesophases. However, at present it is not possible to assign structures. The carboxylates melt to the isotropic liquid phase around 130-150°C. Results on the cerium(III) carboxylates are compared with those for other polyvalent metal ions, and it will be shown that competition between melting of the hydrocarbon chains and coordination of the metal ions are major factors in the phase behaviour.

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### 359.D1 THE KINETICS OF THE MICELLE FORMING SYSTEMS

Evgeniy V. Chertkov, Abdullah A. Saidov, Pulat K. Khabibullaev

*Heat Physics Department of the AS of Uzbekistan, 700135, Katartal str., 28 Tashkent, Uzbekistan.*

The results of the kinetic studies of processes premicellar and, micellar selfassociation in aqueous solutions of a widely-used surface-active substance - sodium decylsulfonate determining the dynamics of the system behaviour have been presented in this work. The low-frequency spectra of various states: premicellar or "precritical", "critical" close to the critical micellization concentrations (CMC) very much and in the field of the concentrations of the substance above CMC have been studied with the methods of modern acoustic experiment within the broad temperature and frequency ranges ( $T = 30^\circ\text{-}60^\circ\text{C}$  and  $f = 60 - 6000 \text{ kHz}$ ). The behaviour of relaxations frequency has shown the possibility of critical description of the micellization process. The energy activations of micellization ( $E_a = 18318 \text{ kJ/mol}$ ) and the constant of dissociations

reaction ( $k_{-1} = 10 - 2.10 \text{ s}^{-1}$ ) have been determined quite correctly. The calculated value of CMC is the same as the one found from experiments on the study of rheological properties.

### 360.D1

#### NMR STUDIES OF LYOTROPIC PHASES OF A NONIONIC SURFACTANT-OIL-WATER SYSTEM

L. Coppola<sup>1</sup>, U. Olsson<sup>2</sup>, C. Oliviero<sup>1</sup>, R. Muzzalupo<sup>1</sup>, G.A. Ranieri<sup>1</sup> and M. Terenzi<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Calabria, 87030 Arcavacata di Rende, Italy

<sup>2</sup>Division of Physical Chemistry I, Chemical Center, Lund University, P.O. Box 124, S221 00 Lund, Sweden

NMR techniques have been used in order to study the microstructures of some lyotropic phases in a ternary system with a nonionic surfactant. The ternary nonionic system contains pentaethylene glycol dodecyl ether ( $\text{C}_{12}\text{E}_5$ ), decane and  $\text{D}_2\text{O}$ , where the surfactant-to-oil ratio 50/50 (w/w) is kept constant.

<sup>2</sup>H-NMR line shape measurements have been carried out to follow the formation liquid crystalline phases. The structural sequence of normal spheres to planar bilayers, via cylinders, was observed as a function of decreasing water concentration at a fixed temperature. Special attention was focused on the lamellar microstructures by changing temperature and composition.

The phase diagram of this ternary system was found similar to that of the binary surfactant-water system.

Accurate measurements of water, oil and surfactant self-diffusion have been performed in lamellar and hexagonal mixtures by using the Fourier Transform Pulsed Gradient Spin-Echo NMR method. The self-diffusion measurements have been interpreted with the one- and two-dimensional diffusional models.

### 361.D1

#### NEUTRON SCATTERING STUDIES OF SHEAR-INDUCED ORIENTATION AND RE-ORIENTATION

T.L. Crowley<sup>1</sup>, C.J. Bottrill<sup>1</sup>, D. Mateer<sup>1</sup>, W.J. Harrison<sup>2</sup>, G.J.T. Tiddy<sup>1</sup>

<sup>1</sup>Division of Chemical Sciences, Science Research Institute, University of Salford, M5 4WT, UK

<sup>2</sup>Research Division W93, Kodak Ltd, Headstone Drive, Harrow, Middlesex, HA1 4TY, UK

Neutron scattering has been carried out on two dye lyotropic liquid crystalline phases, one an azo dye (A) which aggregates in solution to form rods and an hexagonal phase, and the second a cyanine dye (B) which aggregates in sheets forming a layer phase. The dyes were placed in a Couette shear cell so that the influence of shear on the aggregate orientation could be determined. Measurements were carried out with the beam passing through the cell-centre and the cell-side, so that orientation along and at right angles to the flow direction was monitored. Both dyes show some unusual reorientation behaviour. The aggregates of the hexagonal phase are highly ordered along the direction of flow at low shear rate ( $2.78\text{s}^{-1}$ ), with the degree of order being reduced at the highest shear rate ( $1002\text{s}^{-1}$ ). Quite remarkably, on cessation of shear the rods appear to be at right angles to the orientation direction observed for low shear. For the dye B mesophase, the layers are aligned preferentially parallel to the cell walls at low and high shear, although in the latter case the separation between the layers appears to be reduced by ca. 10%. On cessation of shear again we observe that the orientation of the aggregates is very different, with much of the material having layers perpendicular to the cell walls. This is the first report of chromonic mesophase reorientation under shear, and the first time that a shear-induced change in the separation between aggregates has been observed.

### 362.D1

#### MICELLISATION OF QUATERNARY AMMONIUM $\omega$ -HYDROXY BOLAFORM SURFACTANTS

Tim Davey\*, Alan Hayman, William Ducker

Chemistry Department, University of Otago, Dunedin, New Zealand

An analogue of the well studied surfactant cetyltrimethylammonium bromide (CTAB) has been prepared. This compound,



has been shown to form aggregates in solution above its Krafft temperature of 63 °C as determined by  $^1\text{H}$  NMR spectroscopy. The interesting difference between CTAB and  $\text{TMC}_{16}\text{OH}$  is that, whereas CTAB shows one transition (at 1.5 mmol  $\text{L}^{-1}$ ) at 65 degrees from monomers to micelles,  $\text{TMC}_{16}\text{OH}$  shows two transitions (at 6 and 15 mmol  $\text{L}^{-1}$ ).

The electrical conductivity method was used to study the micellisation of  $\text{TMC}_{16}\text{OH}$  and CTAB. Whereas the plot of conductivity versus concentration shows a transition in mobility for CTAB at 65 degrees, the same plot for  $\text{TMC}_{16}\text{OH}$  shows no such transition. The lack of change in mobility of  $\text{TMC}_{16}\text{OH}$  suggests that the solution aggregates are small and/or have a low charge density. This structure could be achieved if both the quaternary ammonium and alcohol functionalities were located on the surface.

$\text{TMC}_{16}\text{OH}$  is surmised to aggregate in a similar fashion to that of the  $\alpha$ ,  $\omega$  - bis(quaternary ammonium) (bis(Quat)) surfactants, whereby both terminal polar portions of the surfactant are positioned on the micelle exterior, in contact with the aqueous medium.

### 363.D1 PROPERTIES AND STRUCTURES OF LYOTROPIC-NEMATIC AND LYOTROPIC-CHOLESTERIC PHASES

H.-D. Dörfler

*TU Dresden, Dresden, Germany*

The formation of lyotropic mesophases in systems of tetradecyldimethyl-aminoxide/ water/aliphatic alcohol was studied in dependence of the chain length of surfactants and aliphatic alcohols. The ternary phase diagrams were established. The following lyotropic phases were formed by microscopic texture observation: Hexagonal phase ( $\text{H}$ ), lamellar phase ( $\text{L}_\alpha$ ), rodlike nematic phase ( $\text{N}_\text{C}$ ) and disclike nematic phase ( $\text{N}_\text{D}$ ). The positions of the corresponding regions in the phase diagrams were fixed. In particular, the  $\text{N}_\text{C}$ - and  $\text{N}_\text{D}$ -phase were of special interest. Lyotropic-cholesteric phases were induced in the lyotropic-nematic phase region by adding optically active compounds. We have focused our attention of chiral compounds. When subjected to the influence of a magnetic field, the lyotropic-cholesteric phase shows the so-called spaghetti-like texture. This texture have been used for determining the pitch length. A linear relation between reciprocal pitch length and concentration of the optically active component was established. The phase behaviour and their alignment in magnetic field of the ternary system hexadecyldimethylethyl-ammoniumbromide/n-decanol/water was investigate by texture observations and small-angle X-ray scattering in order to determine shape, size and micellar aggregation numbers of their aggregates. The shape transformation of the micellar aggregates and changes of their aggregation number of chiral compound with asymmetric C-atom in the lyotropic-nematic matrix are found. Chiral compounds with just one hydrophilic ligand large the micellar asymmetry and induce an chiral shape of micellar aggregates. It seems to us that the chiral elements are located in the head group region of the anisotropic micellar aggregates and diminish their asymmetry. In this case the mechanism of twisting is mainly caused by interaction in pairs of chiral molecules of adjacent micellar aggregates in the lyotropic-cholesteric phase. Hydrophilic inducers of hydrophobic solutes with ionizable groups subjected to strong interactions with the electric double layer in the head group region will originate lyotropic-cholesteric phases whose helical twist sense can be inverted by changes on the charges distribution of the micellar interface.

### 364.D1 MONTE CARLO SIMULATION: SELF-ASSEMBLED LAYERS FROM AMPHIPHILIC MOLECULES ON AND NEAR HOMOGENEOUS AND HETEROGENEOUS SURFACES

A. Drefahl, M. Wahab, O. Seidel, H.-J. Mögel

*Freiberg University of Mining and Technology, Institute of Physical Chemistry,  
D-09596 Freiberg, Germany*

Cubic-Lattice Monte Carlo (CLMC) simulation has been applied to amphiphilic molecules using periodic boundary conditions in x-, y-, and z-direction ( $x,y,z\text{-pbc}$ ) and periodic boundary conditions in x- and y-direction ( $x,y\text{-pbc}$ ) whereas molecule movement in z-direction is limited by one or two impenetrable surfaces. The molecules consist of one head segment followed by a chain of tail segments. This chain may be



unbranched or branched. Each segment occupies one lattice site. Attractive or repulsive interaction energies apply to non-bonded segment pairs on adjacent lattice sites. In addition, interaction energies may be specified for those segments sitting on surface-adjacent sites. Segment-free sites are specified either as non-interacting vacuum sites or as sites occupied by interacting solvent molecules.

We began with CLMC-simulations of monolayers in which the head segments, located on lattice sites adjacent to a homogeneous surface plane, were confined to move in x- and y-direction only. Tail segments were allowed to move above the surface while their moves are restrained by the segment-segment bonds and the excluded-volume condition. Monolayer properties at thermodynamic equilibrium have been studied as a function of head density, chain length, molecular branching, head group structure, layer composition (pure compound or mixture), and segment-segment interaction.

CLMC-simulation with flexible and rigid amphiphiles (one head segment, two to four tail segments) assemble into micellar, bicontinuous, and lamellar nanostructures, depending on molecule concentration and system temperature (M. Wahab). Our ongoing research program is exploring simulations of layer and nanostructure formation in similar systems with one or two surface boundaries. The existing simulation software is currently upgraded with additional modules required for the generation and integration of heterogeneous surfaces. Further, algorithms for the evaluation of adsorption isotherms, for cluster detection, and for percolation analysis are currently designed and tested. The object-oriented programming approach provides us with highly flexible simulations tools that can easily be modified and adapted as soon as new requirements arise from our proceeding simulation studies.

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft through Grant SFB/285 and from the Fond der Chemischen Industrie.

### **365.D1    ROLE OF ION-EXCHANGE IN DETERMINING THE STRUCTURE OF CATIONIC SURFACTANT SURFACE-AGGREGATES**

**William A. Ducker and Erica J. Wanless**

*Department of Chemistry, University of Otago, P. O. Box 56, Dunedin, New Zealand*

Surfactant molecules are known to aggregate at some interfaces as well as in bulk solution. Here we describe an investigation of surface aggregation by Atomic Force Microscopy (AFM). The cationic surfactant, hexadecyltrimethylammonium bromide (CTAB) aggregates into cylindrical structures at the interface between muscovite mica and aqueous solution. We have studied this aggregation in the presence of competing cations.

### **366.D1    SELF-ASSEMBLIES IN MOLECULAR AND MICROHETEROGENEOUS SOLUTIONS: SUPRAMOLECULAR STRUCTURE AND PROPERTIES**

**V. A. Durov**

*Department of Physical Chemistry, Faculty of Chemistry,  
M. Lomonosov Moscow State University, W-234, Moscow, 119899, Russia.*

The interrelations between supramolecular organization of homogeneous molecular solutions (associates, complexes, etc.) and microheterogeneous systems (micelles, microemulsions) are analysed. Problems on the construction of the theory of microheterogeneous systems on the basis of recent development of the models on supramolecular organization and properties of molecular liquids [1] are discussed. The basis of generalized quasichemical approach are reviewed. The hierarchy of the models of supramolecular species mixtures are considered. Models of polyvariable supramolecular species, and the methods for description of their structure, composition, electric (dipole moment) and optical (polarizability tensor) properties, are considered. The interrelations between the macroscopic thermodynamic (Gibbs energy, enthalpy, entropy of mixing), dielectric (static permittivity), optical (refraction index, coefficients of Rayleigh light scattering) properties of liquid solutions, on one hand, and microscopic properties of the supramolecular species, on another, have been analysed. Macroscopic manifestations of the liquid systems supramolecular organization, and important role of the long range structural correlations of molecules in

properties of liquids and solutions are underlined [2]. Problems, concerning the fractal nature of supra-molecular organization and design of new liquid materials are outlined. The role and manifestations of the conformational states of molecules, translation-orientational correlations, structural and phase transitions, etc., in macroscopic properties of microheterogeneous systems (as example - non-ionogenic surface active substances and their solutions) under temperature and composition variations are considered the comparison between approach proposed and traditional phenomenological way, based on the transition from macroscopic heterogeneous systems to the microheterogeneous ones are discussed.

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### 367.D1 THE INTERMEDIATE MESH STRUCTURE IN NON-IONIC SURFACTANT WATER MIXTURES

C. E. Fairhurst<sup>1</sup>, A. S. Fogden<sup>2</sup>, M. C. Holmes<sup>1</sup> and M. S. Leaver<sup>1</sup>

<sup>1</sup>*Department of Physics, Astronomy and Mathematics, University of Central Lancashire, Preston, PR1 2HE, Lancashire, England.*

<sup>2</sup>*Physical Chemistry 1, Lund University, PO Box 124, S-221 00 Lund, Sweden.*

Non ionic surfactant water mixtures are model systems on which to study molecular self assembly into lyotropic liquid crystalline phases. The classical phase sequence observed in such systems is isotropic (micellar) liquid, then hexagonal ( $H_1$ ) followed by lamellar phase ( $L_\alpha$ ). Such topological transitions are driven by the need of the system to reduce interfacial curvature upon increasing concentration or temperature. Much attention has also been focused on the bicontinuous cubic phase which is often found to occur as the structural intermediate between the  $H_1$  and  $L_\alpha$  phases<sup>1</sup>. The structure of the latter phases is now well established and it has been demonstrated that their topology can be successfully fitted to those of periodic minimal surfaces<sup>2</sup>.

Recently it has been demonstrated that the region between the  $H_1$  and  $L_\alpha$  phases can contain lyotropic liquid crystalline phase structures possessing symmetries lower than cubic. These are the so called intermediate phases, which fall into three broad structural classes. These are:

'*Ribbon Phases*', where the structural unit is a micelle with a non circular cross section packed into a regular array<sup>3</sup>;

'*Mesh phases*', where the phase consists of lamellar like bilayers pierced by regular water filled defects whose position is correlated between the layers<sup>4</sup>;

'*Bicontinuous non cubic phases*', for which there are many possible structural variants, of which the cubic phase distorted in one, or more, directions<sup>5</sup> is an example.

In this paper we will summarise the experimental evidence, from many techniques, for two mesh phases formed in non-ionic surfactant water mixtures, which possess rhombohedral symmetry, space group  $R\bar{3}m$ <sup>6,7</sup>. Finally we extend the discussion of these mesh phases by modelling the structure using both 3- and 6- connected surfaces with uniform curvature<sup>8</sup> and demonstrate the importance of balancing local topological constraints with interactions between the layers in the mesh structure.

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### 368.D1 LAMELLAR LIQUID CRYSTALLINE PHASES AND LUBRICATION

S. Fuller, E. Wyn-Jones, R.D. Arnell and G.J.T. Tiddy

*Research Institutes for Science and Design, Manufacture and Marketing,  
University of Salford, Salford, M5 4WT, UK.*

Environmental considerations have prompted a search for novel lubricants made from (cheap) renewable raw materials and that are readily biodegradable and non-toxic. We have examined a series of surfactant lamellar phases in polar non-aqueous solvents (ethylene glycol, glycerol). Such phases occur readily in water as solvent, but these are not usually suitable as lubricants because of corrosion problems and difficulties at elevated temperatures. Over recent years we have developed an understanding of how to obtain these mesophases in other solvents. The lamellar phase is an attractive candidate for a lubrication fluid because the surfactant aggregates (bilayers) bear a strong resemblance to the surfactant layers adsorbed at solid surfaces which are thought to provide a lubricating film. Our studies have concentrated on mixtures of ionic surfactants and unchanged amphiphilic co-surfactants in ethylene glycol as solvent. We have employed the pin on disc, thrust washer and four ball tests to screen lubrication properties. A number of systems have been identified that show lubrication properties matching commercially available products. Preliminary X-ray and neutron diffraction studies on the influence of flow on mesophase structure are under way.

### 369.D1 LAMELLAR-TO HEXAGONAL PHASE TRANSITION IN POPC/C<sub>12</sub>E<sub>n</sub> MIXED SYSTEMS

T. Gutberlet<sup>1</sup>, G. Klose<sup>1</sup>, G. Rapp<sup>2</sup>

<sup>1</sup>*Inst. of Exp. Physik I, Universität Leipzig, Linnéstr. 5, D- 04103 Leipzig*

<sup>2</sup>*EMBL Hamburg Outstation, DESY, Notkestr. 85, D- 22603 Hamburg*

Mixtures of amphoteric phospholipid POPC with surfactants of type C<sub>12</sub>E<sub>n</sub> (n= 2,4) are able to adopt non lamellar phases at reduced hydration (1). The transition of lamellar to hexagonal phase happens on increasing the amount of surfactant in the mixture, increasing temperature or decreasing the relative humidity of the systems. At reduced hydration the transition is of the lamellar L<sub>β</sub> into the inverted hexagonal H<sub>II</sub> phase on increasing the temperature. No intermediate fluid L<sub>β</sub> phase is detected. This phase is found on transformation of the hexagonal phase into the lamellar on increasing the relative humidity of the mixed systems in accordance to the phase diagram established (1).

By time resolved synchrotron diffraction the lamellar-to-hexagonal phase transition and vice versa of POPC/C<sub>12</sub>E<sub>n</sub> (n= 2,4, molar ratio R<sub>L/S</sub>= 0.5) has been studied by temperature and hydration gradients. The mechanism of the transition is found to be a two-state process with broad overlap of both phases during transition but no intermediate phase in the temperature driven transition. Inducing the hexagonal-to-lamellar transition by applying a hydration gradient, a more complex mechanism of nucleation and growth of the fluid lamellar L<sub>β</sub> phase is found, accompanied by the presence of a cubic phase during the transformation (Fig. 1). The different behaviour on temperature and hydration gradients will be discussed and a mechanism of the lamellar-to-hexagonal phase transition in POPC/C<sub>12</sub>E<sub>n</sub> systems presented.

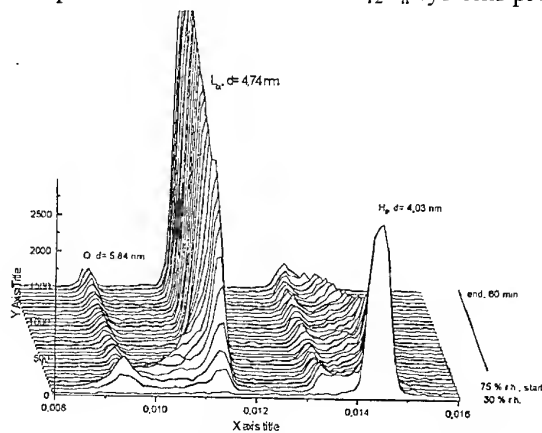


Fig. 1.

## 370.D1

MOLECULAR-ASSEMBLIES IN SYNTHETIC  
GLYCOLIPID/WATER SYSTEMS

How the aqueous phases structures can be controlled by the stereochemistry and the size of their oligosaccharide headgroups ?

Masakatsu Hato<sup>1</sup>, Hiroyuki Minamikawa<sup>1</sup>, Joan.B. Seguer<sup>1</sup>, Kazuyuki Ide<sup>1</sup>, and Yoh Sano<sup>2</sup>

<sup>1</sup>Surface Engineering Laboratory, National Institute of Materials and Chemical Research,  
1-1, Higashi, Tsukuba, Ibaraki-305, Japan

<sup>2</sup>National Food Research Institute, 2-1-2, Kannondai, Tsukuba, Ibaraki-305, Japan

Glycolipids are of great importance both biologically and technically, because of their key roles in recognition processes in biological membranes, and of their potential applications in future biotechnology.

Taking synthetic glycolipids shown in Fig. 1 as examples, we here discuss how the structure of aqueous phases can be controlled by the structural variations of their oligosaccharide headgroups.

For the maltooligosaccharide containing lipid,  $\text{Mal}_N(\text{C}_{12})_2$ , increasing  $N$  in the head groups decreases the hydrated solid/liquid crystalline phase transition temperature,  $T_m$ , and a preference of the liquid crystalline phases changes from an  $\text{H}_{\text{II}}$  [ $\text{Mal}_1(\text{C}_{12})_2$ ] to an  $\text{H}_1$  [ $\text{Mal}_7(\text{C}_{12})_2$ ] via an  $\text{L}_\alpha$  [ $\text{Mal}_7(\text{C}_{12})_2$  with  $N=2,3$ ].  $\text{Mal}_7(\text{C}_{12})_2$  forms normal micelles and becomes water-soluble. On the other hand, the  $T_m$  of the celooligosaccharide containing lipids  $\text{Cel}_N(\text{C}_{12})_2$  increases with increasing  $N$  of the celooligosaccharide headgroups. Since  $T_m$  of  $\text{Cel}_5(\text{C}_{12})_2$  is above 160 °C, it can not form liquid crystalline phase and becomes totally insoluble in water. The results can be explained in terms of different conformations of the headgroups, i.e., a "helical" conformation of the maltooligosaccharides, and an "extended" conformation of the celooligosaccharides.

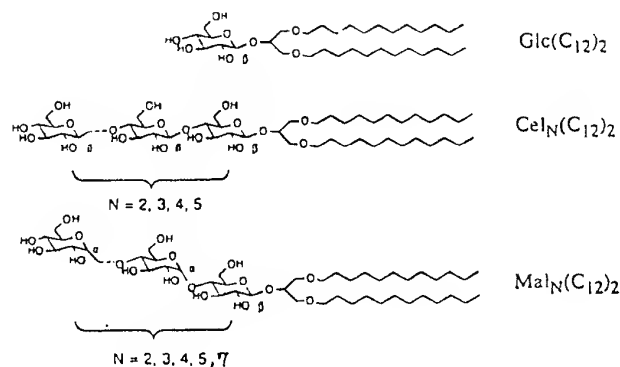


Fig. 1. Chemical Structure of the synthetic glycolipids, 1,3-di-O-dodecyl-2-( $\beta$ -glycosyl)glycerols bearing celooligosaccharides ( $\beta$ -1,4-O-glycosidic bonds) and maltooligosaccharides ( $\alpha$ -1,4-O-glycosidic bonds) as hydrophilic groups.

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371.D1 NMR STUDIES OF THE SOLID CORE AND THE LIQUID CORONA OF A  
SERIES OF PLA:PEG DIBLOCK COPOLYMERS IN THE MICELLAR STATE

C.R. Heald, S. Stolnik, K. Kujawinski, C. De Matteis, M.C. Garnett, L. Illum, S.S. Davis.

Department of Pharmaceutical Sciences, University of Nottingham, Nottingham, England.

Over the last few years, much attention has been given to the study of polymeric nanoparticles as novel drug delivery systems. One of these systems can be obtained when diblock copolymers of poly(lactic acid) (PLA) and poly(ethylene glycol) (PEG) are placed in a selective solvent (water) and micellar structures are formed. The PLA blocks form into a central hydrophobic core, whilst the PEG blocks form into an exterior hydrophilic corona, in which the PEG blocks are in an extended solvated state in a similar way to

classical micellar systems eg, Triton X-100. With the incorporation of hydrophobic drugs into the core of the micelle at preparation time, these micelles can be used as drug delivery agents. The aim of this work was to study the structure and behaviour of these micelles (core and corona) by NMR when they were produced in  $D_2O$  and to compare them to the structure of the PLA:PEG diblock copolymer homogeneously dissolved in  $d_6$ -acetone.

NMR spectroscopic analysis was carried out on a series of PLA:PEG diblock copolymers (Mw PEG 5kDa, Mw PLA 2, 3, 4, 6, 10, 13 and 25kDa) in order to examine how the structure of both the micellar core and corona alters as the PLA block increases in size.

$^1H$  NMR studies at 250MHz have been performed. In  $d_6$ -acetone, complete resolution of the PLA and PEG blocks was seen, whilst in  $D_2O$ , the methine (CH) and most of the methyl ( $CH_3$ ) peak was not seen. This suggests that the PLA forms a central solid-like core, with the PEG forming a mobile outer corona of the micelle. For the smaller PLA:PEG micelles (2:5, 3:5 and 4:5) more of the central PLA core is seen indicating some liquid-like behaviour of the core. This observation shows that the micelle structures became more rigid with increasing size of the PLA block. In the PLA:PEG series, the PEG peak is consistently seen (broad singlet at 3.68ppm) suggesting mobility of this moiety which must be on the surface of the micelle. Quantitative analysis of the PEG corona layer using an internal standard showed that all of the PEG protons were seen during the NMR experiments, suggesting that all the PEG is in a liquid state and not trapped in the central solid core of the micelle.

NMR experiments above room temperature showed that as the temperature increases, more of the CH and  $CH_3$  groups were seen. At 70 °C most of PLA portion was seen as multiplets at ~1.5 ppm ( $CH_3$ ) and ~5.5ppm (CH) respectively.  $^{13}C$  solid state NMR studies show the central PLA core (methyl signal) as two distinct signals. Firstly, a broad peak indicates a relatively rigid region and secondly two sharp peaks indicate a more mobile region of the core at the PLA/PEG interface. The solid state NMR also indicates the presence of a mobile corona region.

In summary, these various NMR experiments have shown the solid-like, rigid structure of the central PLA core of these micelles, together with the mobile nature of the PEG corona layer. All the PEG was observed at room temperature, whilst the PLA core is only seen at elevated temperature. Furthermore, we have seen a small amount of the PLA blocks in a mobile liquid-state at the interface between the two layers.

We would like to thank S. Purkiss and N. Bateman at Zeneca Pharmaceuticals, Alderley Edge for the synthesis of the PLA:PEG diblock copolymers used in this study.

## 372.D1

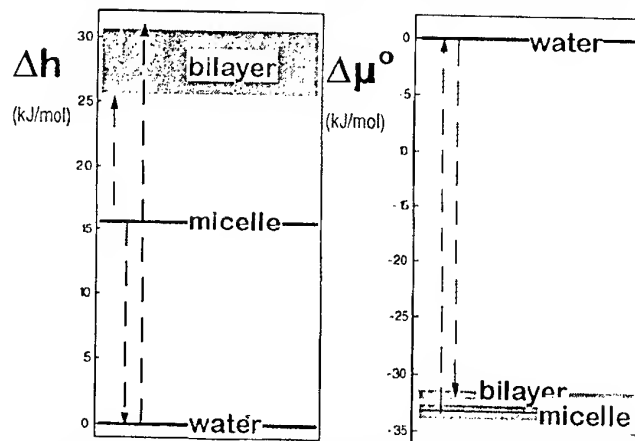
### LIPID/DETERGENT INTERACTION THERMODYNAMICS SEEN BY ISOTHERMAL TITRATION CALORIMETRY

H. Heerklotz, H. Binder, G. Lantzsch, G. Klose

*Institut für Experimentelle Physik 1, Universität Leipzig, Germany*

How do detergents partition between lipid membranes and the aqueous medium? Which generalized forces of enthalpic as well as entropic nature control the incorporation of detergents into pure and mixed aggregates? How much detergent can a membrane "stand" until it is solubilized, and which are the physical or molecular parameters determining this critical fraction? What are the molecular origins of the interaction forces, which role play packing, hydration or dipole interaction?

These questions are important for a lot of purposes, from the choice of suitable detergents for a given application up to general insights into the nature of inter-actions determining the function of a biological membrane. Isothermal titration calorimetry can yield very important information to (at least partially) answer the above questions. A number of experimental protocols and a model for the interpretation of all the experimental data in terms of transfer heats are given in Heerklotz et al., J.Phys. Chem 1996,100,6764. To understand the meaning of



Example: Transfer enthalpy  $\Delta h$  and standard chemical potential difference  $\Delta\mu^0$  of the detergent  $C_{12}EO_8$  between water, micelles and POPC bilayers (of varying composition) at 25 °C

these thermodynamic quantities on a molecular level, one needs to consider as much as possible different detergents and lipids. For example, systematic studies with POPC and the homologue series  $C_{12}EO_n$  ( $n=3-8$ ) showed the importance of packing properties, i.e. molecular shapes or spontaneous curvatures, for the thermodynamics of mixed lamellar as well as micellar aggregates.

### 373.D1 PHASE BEHAVIOR AND MICROSTRUCTURES IN SURFACTANT MIXTURES

**Eric W. Kaler and Daniel J. Iampietro**

*Center for Molecular and Engineering Thermodynamics, Department of Chemical Engineering, Colburn Laboratory, University of Delaware, Newark, DE 19716 USA*

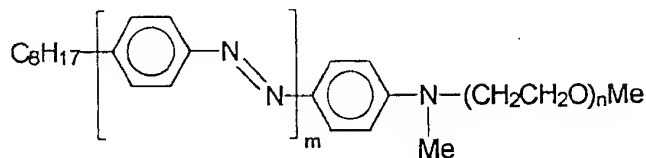
We have found that the electrostatic interactions of anionic and cationic surfactants makes available a rich variety of microstructures. In particular, unilamellar vesicles form spontaneously in a number of anionic/cationic surfactant mixtures. This is especially interesting in the case of mixtures of fluorocarbon and hydrocarbon surfactant, where in addition changes in structures with temperature is also observed. Here we present results for various mixtures of surfactants and explore the range of micellar, precipitate and vesicle phases. Micellar solutions spontaneously transform into vesicular solutions with dilution in the vicinity of the critical micelle concentration of the predominant surfactant. This transformation is abrupt and reversible. The results are organized and understood in terms of a thermodynamic cell model of the Gibbs free energy of various phases. Small angle neutron scattering measurements confirm a variety of model predictions about aggregate size and composition.

### 374.D1 SELF - ASSEMBLY OF OLIGOMERIC AZOBENZENE AMPHIPHILES

**Tomasz Kozlecki, Kazimiera A. Wilk**

*Institute of Organic and Polymer Technology, Technical University of Wrocław, Wyspińskiego 27, 50-370 Wrocław, Poland*

Oligomeric azobenzene derivatives of a general structure:



have been synthesized and their self-aggregation behavior in water and carbon tetrachloride have been studied by means of electron and nuclear magnetic resonance spectroscopy. Their photochemical behavior, especially reversible photoisomerization, has been described in both homogeneous and constrained systems.

### 375.D1 CHARACTERISATION OF SELF-ASSEMBLED PHOSPHOLIPID MONOLAYERS AND BILAYERS

**G.A. Lawrie, G.T. Barnes and I.R. Gentle**

*Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia*

Phospholipids may spontaneously form monolayers at the air/water interface and bilayer structures (liposomes) in aqueous dispersions (1,2). A monolayer at the air/water interface can be formed from a

variety of sources such as anhydrous crystalline material or dispersed liposomes of varying size and nature. The stable surface pressure established by the monolayer upon self-assembly varies according to the nature of the source (2,3), and the rate of monolayer formation also varies (2). In addition, recent studies (4) of the isotherms of these monolayers have shown that the compressional behaviour in the liquid condensed region is dependent on the source of the monolayer. It is therefore desirable to examine such self-assembled films to discern any differences in structure.

The structures of self-assembled monolayers and bilayers of dimyristoyl and dipalmitoyl phosphatidylcholine (DMPC, DPPC) have been studied by scanning probe techniques. The floating monolayers were prepared by spreading from a remote reservoir via a bridge (after Heyn, Egger and Gaub (5)). The sources were anhydrous bulk crystals, multilamellar vesicles, small unilamellar vesicles and large unilamellar vesicles. The monolayers were deposited on a variety of substrates by the horizontal (Langmuir-Schaefer) dipping method using both hydrophilic and hydrophobic substrate surfaces. These films were then characterised by atomic force microscopy. Images are presented to illustrate the differences between the self assembled films formed from the different sources.

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### 376.D1

#### DYNAMICS OF MICELLES OF POLYOXYETHYLENE-POLYOXYPROPYLENE-POLYOXYETHYLENE BLOCK COPOLYMERS IN AQUEOUS SOLUTIONS

Bernard Michels<sup>1</sup>, Gilles Waton<sup>1</sup> and Raoul Zana<sup>2</sup>

<sup>1</sup>Laboratoire d'Ultrasons et de Dynamique des Fluides Complexes, URA 851 du CNRS, Université Louis Pasteur, 4, rue Blaise Pascal, 67070, Strasbourg-Cedex, France

<sup>2</sup>Institut C. Sadron (CNRS-ULP), 6, rue Boussingault, 67083, Strasbourg-Cedex, France

This study is the first comprehensive one of the dynamics of block copolymer micelles in aqueous solution. The dynamics of the micelles of two triblock polyethyleneoxide-polypropyleneoxide-polyethyleneoxide copolymers, the Pluronics EO<sub>13</sub>PO<sub>30</sub>EO<sub>13</sub> (L64) and EO<sub>73</sub>PO<sub>27</sub>EO<sub>73</sub> (PF80) has been investigated using the temperature-jump (T-jump) and the ultrasonic relaxation methods. The ultrasonic absorption measurements revealed the existence of a relaxation process which was assigned to the exchange of copolymer between micelles and intermicellar solution. The T-jump experiments revealed two slower relaxation processes, with the faster one dependent on the scattering angle. This process was assigned to the effect of Pluronic exchange on fluctuations of Pluronic micelle concentration. The slow T-jump process gave rise to a *decrease* of intensity and was attributed to the return to equilibrium of the micelle size distribution involving an increase in micelle number. Overall, the kinetics of block copolymer micelles follows the scheme proposed by Aniansson and Wall for conventional surfactants with a response of the micellar systems to a fast perturbation characterized by two time constants, one for the fast change of micelle aggregation numbers at nearly constant number of micelles (exchange process), the other for the adjustment of the micelles numbers to the final micelle size distribution (micelle formation/breakup). The association of the Pluronic L64 to its micelles is nearly diffusion-controlled. The micelle formation/breakup process appears to proceed via reactions of fission/fusion, as in the case of nonionic ethoxylated surfactants. These results demand to be extended to other Pluronic copolymers in order to assess their degree of generality.

### 377.D1      STRUCTURAL PROPERTIES OF POLYDISPERSE MICELLAR SOLUTIONS

Elena Mileva

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, "Acad.G.Bonchev" bl.11,  
Sofia 1113, Bulgaria*

A detailed model for the static structural characteristics of polydisperse self-assembling solutions in the semidilute regime, far from the liquid crystalline phase-transitions points is proposed. Micellar systems containing elongated aggregates formed by ionic amphiphiles in the presence of added salt are studied. Important structural characteristics of the self-assembling species, namely the interaction potentials of the various aggregates, the radial distribution functions of the respective entities, etc., are properly defined. The structural peculiarities are determined by effective potentials including the screened electrostatic and the hard-core interactions. A procedure is applied for the expansion of the characteristic parameters of the system around a suitable reference system. The latter is an imaginary solution of polydisperse spherical micelles. Expressions for the distribution functions show the tendencies for the structural peculiarities of these solutions. The basic result is model size distribution curve that accounts not only for the inherent polydispersity of the system but also includes the interaggregate interactions and the space correlations of the aggregates.

### 378.D1      SELF-ASSEMBLED STRUCTURES IN THIN LIQUID FILMS

Elena Mileva, Dotchi Exerowa

*Institute of Physical Chemistry, Bulgarian Academy of Sciences,  
"Acad.G.Bonchev" bl.11, Sofia 1113, Bulgaria*

The experimental investigations of microscopic thin liquid films reveal that at definite conditions the so-called 'black dots' may be observed. These are miniature nonspreading spots with radius about  $5 \cdot 10^{-4}$  cm. They appear at concentrations of the amphiphilic substance that are considerably lower than the starting value of the usual black-spot and black-film formation. The probability of the onset of the 'dots' in foam films stabilised with sodium dodecylsulphate (SDS) is experimentally investigated for a broad range of the surfactant's concentrations. The probability curve allows the following theoretical interpretation: A series of premicellar structures with various geometries are formed near the interfaces and inside the thin film. Upon increase of the amphiphile quantity, the number, the size and the form of the different self-assembled entities are changed. Some of them are adsorbed at the film surfaces. At particular concentrations, the structures on the film interfaces begin to interact. This may lead to the onset of local thinning that is registered as 'black dot'.

The proposed treatment is the first attempt to connect the onset of 'black dots' with the presence of the amphiphilic self-assembled structures in thin films. Thus it is shown that the microscopic thin-film investigations are very suitable for the identification and the study of premicellar entities in the vicinity and at fluid interfaces.

### 379.D1      EFFECTS OF PRESSURE ON THE MICELLIZATION OF TETRADECANE-1-SULFONATES WITH DIVALENT CATION OF SEPARATE ELECTRIC CHARGES AS COUNTERION\*

Yoshikiyo Moroi<sup>1</sup>, Yoshio Murata<sup>2</sup> and Mitsuru Tanaka<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812-81, Japan;

<sup>2</sup>Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka 814-80, Japan

The effects of pressure on the solution properties of tetradecane-1-sulfonates with divalent cation of separate electric charges as counterions (1,1'-(1, $\omega$ -alkanediyl)bispyridinium tetradecane-1-sulfonate) were examined at 40°C by the critical micelle concentration (CMC) and by the aqueous solubility. Specific



conductivity of the surfactants below the CMC was found to increase monotonously with pressure. Long-chain surfactant anions would thus appear to associate with the divalent cations below the CMC, the extent of which decreasing with increasing pressure. The CMC of all surfactants was found to have a maximum around 140MP as conventional ionic surfactants. The volume change on micellization,  $\Delta V_m$ , was determined based on the pressure dependence of CMC, and  $\Delta V_m$  was observed to decrease more rapidly with pressure for shorter charge separation of the counterions. Dynamic light scattering was measured for micellar solutions, and the results indicated the hydrodynamic radius of micelles to be considerably controlled by divalent cationic counterions of increasing charge separation.

\* J. Jpn. Oil Chem. Soc., 45(7), 627(1996).

### 380.D1 MESOMORPHIC BEHAVIOUR OF N-(n-ALKYL)PYRIDINIUM HYDROGENSULFATES

Annerose Müller, Irmtraut Stella

*Ernst-Moritz-Arndt-University, Greifswald, Institute of Organic Chemistry*

The mesophase behaviour of a homologous series of N-(n-alkyl) pyridinium hydrogensulfates has been examined by thermal and optical studies. These cationic surfactants don't form only thermotropic mesophases at relative low temperatures (about 100°C) but they also form lyotropic mesophases in the unconventional solvent concentrated sulfuric acid.

The DSC-traces of the pyridinium hydrogensulfates display two peaks with large enthalpy changes. At the first transition temperature  $T_{m1}$  no fluid mesophase is detectable. Only at the second phase transition temperature  $T_{m2}$  a birefringent melt with mesomorphic structures is observed. That means, the low temperature phase transition  $T_{m1}$  is a change between two solid modifications. The mesophase behaviour depends on the chain length  $n$  of the alkyl chain.

The N-(n-alkyl)pyridinium hydrogensulfates don't form only anhydrous thermotropic mesophases but also lyotropic ones in concentrated sulfuric acid.

The phase types have been monitored using the polarizing microscope penetration technique. This provides rapidly a qualitative overview of the mesophase sequences. All the phases could be distinguished by the refractive-index discontinuities at their boundaries. While only hexagonal and lamellar phases can be seen between crossed polarizers due to the birefringence, cubic phases can be distinguished by the non-spherical air bubbles, due to the high viscosity of these phases.

The sequences of lyotropic liquid-crystalline phases occurring in aqueous solutions of cationic surfactants also appear in surfactant/conc.  $H_2SO_4$  systems. Thus for  $n = 18$  on increasing surfactant concentration in conc.  $H_2SO_4$  mesophases occur in the following sequence:

micellare solution ( $L_1$ )  $\rightarrow$  cubic ( $I_1$ )  $\rightarrow$  hexagonal ( $H_1$ )  $\rightarrow$  cubic ( $V_1$ )  $\rightarrow$   
lamellar ( $L\alpha$ )  $\rightarrow$  crystalline phase (C).

While at low temperature ( $< 6,5^\circ C$ ) only the cubic  $I_1$ -phase is detectable, with increasing temperature a hexagonal phase  $H_1$  becomes evident and at  $68/69^\circ C$ , another cubic phase  $V_1$  can be identified. The lamellar phase  $L\alpha$  appears not below  $92^\circ C$  whereas the, cubic  $I_1$ -phase is not detectable at this temperature.

The shorter the alkyl chain the fewer lyotropic mesophases are detectable. For  $n=16$  the following sequence can be observed:  $L_1 \rightarrow I_1 \rightarrow H_1 \rightarrow V_1 \rightarrow C$  and for the shortest alkyl chain  $n=12$  only the  $H_1$ -phase exists.

It is a pleasure to acknowledge the help and comments of K.Kratz and D. Sirnon of the Inst.f. Makromol. Chemie, Univ. Freiburg and of O. Dietsch of the I. Stransky Inst., TU Berlin. This work was supported by the Deutsche Forschungsgemeinschaft.

**381.D1****SHEAR INDUCED STRUCTURAL REORGANISATION  
OF LYOTROPIC MESOPHASE****J. Odell<sup>1</sup>, R. Nicol<sup>2</sup>, A. Terry<sup>1</sup>, G. J. T. Tiddy<sup>2</sup> and J. Wilson<sup>3</sup>**<sup>1</sup>*Department of Physics, University of Bristol*<sup>2</sup>*Division of Chemical Sciences, University of Salford*<sup>3</sup>*Unilever Research, Port Sunlight*

The occurrence of lyotropic mesophases is common place in surfactant products. Most product processing involves the flow of multi-phase systems, including mesophases, hence an understanding of their rheology is essential to control product form. We have made rheological measurements for several common surfactant mesophases containing commercial surfactants as a precursor to studying their structural reorganisation under flow. An optical microscope shear cell (Linkam-Cambridge) has been used to monitor mesoscopic structural changes during shear flow using the changes in birefringent optical textures. In addition, low angle X-ray diffraction has been used to determine phase transitions and aggregate dimensions within the phases. Examples of data to illustrate these will be present.

**382.D1 PHASE BEHAVIOR OF POLYOXYETHYLENE OLEYL ETHER IN WATER****Kazuyo Ozawa<sup>1</sup>, Kazuki Shigeta<sup>1</sup>, Masao Suzuki<sup>2</sup>, and Hironobu Kunieda<sup>1</sup>**<sup>1</sup>*Division of Artificial Environments Systems, Graduate School of Engineering,**Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240, Japan*<sup>2</sup>*Oleochemical Research Laboratory, NOF Corporation, Oohama-cho 1-56, Amagasaki 660, Japan*

The variety of self-organizing structure tends to be rich by using long-lipophilic-chain surfactant. However melting temperature of the surfactant increases and some organizing structures would be missing in the longer-chain surfactant systems. Phase diagrams of water-polyoxyethylene-type nonionic surfactant systems were usually constructed as a function of temperature because these surfactants become lipophilic with increasing temperature. Since liquid crystals tend to melt at high temperature, it is hard to find the reverse type of liquid crystal (for example reverse hexagonal liquid crystal) in the binary systems.

In order to solve these problems, we constructed the phase diagram of water-polyoxyethylene oleyl ether system as a function of oxyethylene chain at 25 °C. The present nonionic surfactants have highly pure oleyl group (99.7 %) and their melting temperature is low. Although oleyl surfactants of different polyoxyethylene chains are mixed to construct the phase diagram, it is considered that the phase diagram is not largely influenced by the distribution of oxyethylene chains except in a extremely dilute region. In the phase diagram the phase behavior is very rich, and lamellar and hexagonal liquid crystals, several cubic phases, a sponge phase, and even reverse hexagonal liquid crystal appear. The correlation between HLB (hydrophile-lipophile balance) of the surfactant and the phase behavior is discussed. We will also discuss the effect of polyoxyethylene chain length of the oleyl surfactant on the spontaneous curvature of surfactant layer in self-organizing structures by using the packing equation.

**383.D1****ORIENTATION TRANSITION IN A FERROSMECTIC PHASE  
UNDER MAGNETIC FIELD****Virginie Ponsinet, Pascale Fabre***Laboratoire de Physique de la Matière Condensée, URA-CNRS 792, Collège de France,**11 pl. M. Berthelot, 75005 Paris, France*

A ferrosmectic is a lyotropic lamellar phase in which nanometric magnetic particles are incorporated between the surfactant membranes. These phases possess a strong anisotropy of magnetic susceptibility and undergo spectacular orientation transitions when submitted to weak external magnetic field. In analogy with models of instabilities under external field in thermotropic smectics, we propose a description of the observed phenomena in terms of a phase transition. The critical field corresponding to the transition is

calculated and compared to our experimental results. The model takes into account the binary nature of the system making possible the occurrence of a first-order type transition and includes a detailed description of the elastic and magnetic energies involved in the distortion. We thus explain the observed mechanism of torical defect formation rather than homogeneous instability.

An interesting result of this study is a measurement of the elastic constants of bending and compression of the ferrosmectic phases as a function of the particle volume fraction.

### 384.D1

#### DOMINATING INFLUENCE OF CHAIN LENGTH AND SALT CONCENTRATION ON BLOCK COPOLYMER MICELLIZATION

**Timo Rager, Wolfgang H. Meyer, Gerhard Wegner**

*Max Planck Institut für Polymerforschung, 55128 MAINZ, Germany*

Three pairs of end-labeled, almost symmetric poly(acrylic acid-*b*-methyl methacrylate) block copolymers were synthesized to study micelle formation in water by direct non-radiative energy transfer (DET). One member of each pair contained naphthalene as the donor chromophore at the PMMA chain end; and the other, pyrene as the acceptor. The highest molecular weight sample (70 MMA units) formed micelles even at the lowest concentration of 0.1 mg/L, and did not undergo chain exchange on the time scale of weeks. For its micelle formation in the case of direct dissolution in water with one equivalent NaOH we postulate a fragmentation of the polymer powder instead of an association of single block copolymer chains. The samples with 40 or 20 MMA units are largely dissociated in pure water. The polymer concentration has only a minor effect on aggregation. However, already at low polymer concentration (several mg/L), addition of small amounts of salt (NaCl) strongly promotes the micelle formation. The presence of salt also slows down the exchange rate of the macromolecules among the micelles.

### 385.D1

#### SOME PROPERTIES OF LYOTROPIC HEXAGONAL PHASES INCORPORATING PARTICLES OF NANOMETRIC SIZE

**L. Ramos<sup>1</sup> and P. Fabre<sup>2</sup>**

<sup>1</sup>*Laboratoire de Physique de la Matière Condensée, Collège de France, 11, Pl. Marcelin Berthelot, 75231 Paris Cedex 05, France*

<sup>2</sup>*UMR CNRS-Elf Atochem, 95 rue Danton, 92303 Levallois-Perret Cedex, France*

We have evidenced the existence of "swollen" lyotropic hexagonal phases in a quinary system of oil, water, salt, ionic surfactant and cosurfactant. The swelling consists of an increase of the diameter of the oily cylinders, the control parameter being the ionic force of the polar medium, which directly governs the spontaneous radius of curvature of the surfactant monolayer; cylinders whose diameter can be monitored between 3 and 34 nm, keeping small the distance between adjacent cylinders are thus obtained.

We elaborate a magnetic hexagonal system by incorporating ferrimagnetic particles of typical size 10 nm inside the cylinders of the swollen lyotropic hexagonal phase. The small-angle X-ray scattering spectra of the hybrid systems thus realized display specific features, due to the unidimensional confinement of the gas of colloidal particles.

Moreover, owing to the magnetic nature of the particles, the hybrid system reorient under a weak magnetic field. This property allows to obtain well-oriented samples. They enable the study of the elastic properties of the doped hexagonal phase by means of two experimental techniques. On one hand, by observation of the textures in polarized light microscopy, we determine a penetration length which characterizes the softness of the system. On the other hand, quasi-elastic light scattering experiments give information both on the anisotropic diffusion of the colloids inside the cylinders and on the fluctuations of the cylinders via a hydrodynamic coupling.

**386.D1****THE INFLUENCE OF GELATIN ON THE TWO PHASE  
REGION OF DDAB****Friduddin Rana<sup>1</sup>, Gordon J.T. Tiddy<sup>1</sup>, Jason Gray<sup>1</sup>, William J. Harrison<sup>2</sup>**<sup>1</sup>*University of Salford, Science Research Institute, Salford M5 4WT, UK*<sup>2</sup>*Kodak European Research, Headstone Drive, Harrow, Middlesex HA1 4TY, UK*

The lamellar ( $L_\alpha$ ) mesophase is the structural unit of detergents as well as forming the basic unit of biological membranes. DDAB, didodecyldimethylammonium bromide, exhibits a partial miscibility loop within which two  $L_\alpha$  phases coexist. They are the concentrated and dilute  $L_\alpha$ . We have examined the influence of digel (deionised gelatin) on the occurrence of the two  $L_\alpha$  phases using deuterium NMR and small angle X-ray scattering (SAXS). Three different concentrations of DDAB have been examined, 63%, 60% and 40% DDAB under the influence of 2% and 4% digel.

SAXS had shown that above 80°C for 63% and 60% DDAB (in water), a single concentrated  $L_\alpha$  phase exists. The temperature at which the dilute phase formed had been 70°C. Deuterium NMR however, had shown this temperature to be 77°C. With the addition of digel, two  $L_\alpha$  phases formed at even higher temperatures. On the other hand, 40% DDAB formed a single  $L_\alpha$  phase at 70°C and the temperature in which the concentrated phase formed was 35°C. This increased to 40°C and 50°C when 2% and 4% digel had been added. A third phase had been seen with digel showing the existence of a very dilute  $L_\alpha$  phase.

DDAB can only incorporate a certain amount of gelatin into its  $L_\alpha$  layers and therefore a third phase is produced in which the excess gelatin remains.

Recent results using Neutron Scattering and Stopped Flow combined with SAXS will also be shown.

**387.D1****MONTE CARLO SIMULATIONS OF MOLECULAR SYSTEMS WITH  
PURE REPULSIVE INTERACTIONS: FORMATIONS OF SELF ASSEMBLED STRUCTURES****O. Seidel<sup>1</sup>, P. Schiller<sup>2</sup>, M. Wahab<sup>2</sup>, H.-J. Mögel<sup>1</sup>**<sup>1</sup>*Freiberg University of Mining and Technology, Institute of Physical Chemistry, Leipziger Strasse 29,  
D-09596 Freiberg, Germany*<sup>2</sup>*Martin Luther University Halle-Wittenberg, Institute of Physical Chemistry, Mühlpforte 1,  
D-06108 Halle, Germany*

In aqueous media, the hydrophobic parts of amphiphilic molecules tend to aggregate in order to shield each other from the solvent. This aggregation process mediates the formation of various structures. Despite experimental evidence about self-association in systems containing amphiphiles, it is difficult to explain the details of the clustering process as well as the size, shape and stability of the aggregates. Computer simulation of simple models may increase the theoretical understanding of the clustering process and the shape of the resulting clusters. Although these simple models will not completely reproduce experimental results, they allow to identify the important factors contributing to the clustering process and to the macroscopic properties of the system. Aggregation is observed in simulations of molecular systems which ignore internal water structure and are based entirely on repulsion between hydrocarbon chain segments and solvent. The repulsive force can be interpreted as an effective result of the interplay between energy and water entropy loss which drives aggregation.

In our simulations, single amphiphilic molecules are modelled by self-avoiding random walks on a cubic lattice of edge length  $L$  with  $L^3$  lattice sites. Single molecules (chains) always occupy adjacent sites of the lattice. Periodic boundary conditions are employed. All chains obey the excluded volume criterion. Each chain segment represents several atoms of a real amphiphilic molecule, its type is "head-like" (hydrophilic) or "tail-like" (hydrophobic). If "tail-like" segments are adjacent (nearest neighbour) to solvent sites, pairwise-additive repulsive interactions are taken in consideration. Repulsive intermolecular interactions exist between adjacent but not connected "head-like" and "tail-like" segments and are also pairwise additive.

Each simulation starts at concentration  $c = N.n/L^3$  by placing  $N$  chains of length  $n$  randomly on the lattice, no initial structure is imposed on the chains. The remaining  $\omega = L^3 - N.n$  sites on the lattice represent solvent molecules.

The simplest model of an amphiphilic molecule in a cubic lattice according to the concept above is a chain consisting of one "hydrophilic" head segment connected to one "hydrophobic" tail segment. Due to its compact shape and intrinsic rigidity no micelles form at any concentration. The formation of concentration depended bilayer patches and percolating bilayers is shown via cluster size distribution and orientational order in the concentration-temperature diagram and by pictures of characteristic configurations. Systems composed of flexible and rigid amphiphiles with longer tails converting 2-4 segments and longer heads show concentration and temperature depended structural transitions by assembling into micellar, bicontinuous and lamellar microstructures.

Bolaform amphiphiles are molecules containing two hydrophilic moieties connected by a hydrocarbon chain. It has been shown that bolaform amphiphiles have unusual aggregatin behaviour in lyotropic phases. Simulations with systems consisting of amphiphiles consisting of two heads connected by 4,5 or 6 chain segments have been performed. Bolaform systems exhibit transitions to lamellar phases at lower concentrations compared to conventional amphiphiles. The ratio of extended (bilayer spanning) to folded conformations in dependence of temperature and amphiphile concentration is reported.

In order to characterise the phase behaviour of the systems above, cluster shape, orientational order of the chains in each cluster, center-of-mass positional correlation, and other geometrical and thermodynamical properties have been analysed.

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### **388.D1      PHASE TRANSITION BETWEEN HEXAGONAL-LAMELLAR REVERSE HEXAGONAL LIQUID CRYSTALS IN POLYOXYETHYLENE OLEYLETHER IN WATER**

**Kazuki Shigeta<sup>1</sup>, Kazuyo Ozawa<sup>1</sup>, Masao Suzuki<sup>2</sup>, Hironobu Kunieda<sup>1</sup>**

<sup>1</sup>*Division of Artificial Environments Systems, Graduate School of Engineering,*

*Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240, Japan*

<sup>2</sup>*Oleochemical Research Laboratory, NOF Corporation, Oohama-tyo1-56, Amagasaki 660, Japan*

Various self-organizing structures are formed in a water-polyoxyethylene oleyl ether system. Phase transition from hexagonal liquid crystal to lamellar liquid crystal was investigated by changing the polyoxyethylene chain length at constant temperature. The surfactant contains highly pure oleyl group (more than 99.7%). The change in interlayer spacing of each liquid crystal was by small-angle x-ray scattering (SAXS) at constant volume fraction of lipophile (oleyl) group in the system at 25°C. The volume fraction ratio of hydrophilic part (oxyethylene chain+water) and lipophilic chain (oleyl group) is kept constant (4:1). The interlayer spacing in hexagonal liquid crystal gradually increases with decreasing polyoxyethylene chain and jumps to a high value for lamellar liquid crystal at the transition point. If it is assumed that hexagonal liquid crystal consists of indefinitely long rods, the radius of the rod increases and approaches the length of oleyl chain in the extended form at the transition point. However, the thickness of the lipophilic part in the lamellar liquid crystal is much shorter than that in the extended form. We will discuss the mechanism of the phase transition between the two liquid crystals.

The lamellar liquid crystal is also changed to reverse hexagonal phase via a cubic phase with the further decrease in oxyethylene chain length. The structural change will be also reported.

## 389.D1

SELF-ASSEMBLY OF HIV-1 NUCLEOCAPSID PROTEIN  
NCp7/RNA COMPLEXESS.P. Stoylov<sup>1</sup>, E. Stoylova<sup>1</sup>, C. Vuillenmier<sup>2</sup>, B.P. Roques<sup>3</sup>, Y. Mely<sup>2</sup>, E. Le Cam<sup>4</sup> and D. Gérard<sup>2</sup><sup>1</sup>*Institute of Physical Chemistry, Bulagian Academy of Sciences, 1113 Sofia, Bulgaria*<sup>2</sup>*Laboratoire de Biophysique, URA 491 du CNRS, Faculté de Pharmacie, 74, Route du Rhin,  
B.P. 24, 67401 Illkirch Cedex, France*<sup>3</sup>*Département de Chimie Organique, INSERM U266, CNRS UA 498, U.F.R. des Sciences  
Pharmaceutiques et Biologiques, 4, avenue de l'Observatoire, 75270 Paris Cedex 06, France*<sup>4</sup>*Microscopie Cellulaire et Moléculaire, Institute Gustav Roussy, Rue Camille Desmoulins,  
94805 Villejuif Cedex, France*

Quasielastic light scattering (QELS), fluorescence and optical absorbance studies of interacting HIV-1 nucleocapsid protein NCp7 with RNA show that stable dispersion of almost monodisperse particles appear. The dimensions ( $d$ ) and the composition ( $r_{agg}$ ) of the nucleoprotein particles strongly change with the molar ratio polynucleotide to protein ( $r$ ), protein concentration [NCp7] and salt concentration [NaCl] in a narrow interval of these parameters. The assembly kinetics are well described by power law dependences often used in the analysis of the initial stages of the crystal growth. The parameters of these dependences  $d=at^n$  (the coefficient  $a$  related to the particle properties and power  $n$ , related to the rate and mechanism of particle growth) change in a way similar to that of  $d$  and  $r_{agg}$  with  $r$ , [NCp7] and [NaCl]. The morphology of the particles changes considerably for values of the parameters before and after the interval where the strongest variations of  $d$ ,  $r_{agg}$ ,  $n$  and  $a$  are observed. The mechanism of assembly is discussed on the basis of the observations and possible application to the understanding of biological nucleoprotein particles (viruses, ribosomes, etc.) assembly is discussed.

390.D1 HIGH-ORDER PHASE TRANSITION OF LAMELLAR LIQUID CRYSTAL  
FOR DIALKANOYLPHOSPHATIDYLGLYCEROL SODIUM SALTS IN WATERKazuo Tajima<sup>1</sup>, Masakatsu Koshinuma<sup>2</sup>, Yoko Imai<sup>1</sup>, and Akio Nakamura<sup>3</sup><sup>1</sup>*Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama-shi 221, Japan*<sup>2</sup>*Faculty of Informatics, Teikyo Heisei University, Uruido, Ichiharashi, Chiba 290-01, Japan*<sup>3</sup>*School of Design and Architecture, Nagoya City University, Kitachikusa, Chikusa-ku,  
Nagoya-shi 464, Japan*

A high-order phase transition in the lamellar liquid crystal has been recently found at the  $T^*$ -temperature above the gel-liquid transition temperature,  $T_m$ , of dimyristoylphosphatidylcholine- $H_2O$  system. For this transition a new explanation based on a molecular mechanism has been proposed<sup>1</sup>. Though the  $T^*$ -temperatures for the lamellar liquid crystals of dilauroylphosphatidylglycerol (DLPG) and dimyristoylphosphatidylglycerol (DMPG) sodium salts in water have been also determined as 19.5°C for DLPG and 31.7°C for DMPG<sup>1</sup>, the thermal properties of these lipids bilayers without additive salts have not yet been clear. In this paper, changes in physicochemical states of these lipids have been intensively investigated as a function of incubation time after preparation of the dispersions below and above  $T^*$ . The main measurements were performed by the X-ray diffraction method and the differential scanning calorimetry (DSC).

When the dispersions had been incubated below  $T^*$  for a day after preparation, the repeat distance of the bilayer was 4.2-3 nm (DLPG) or 4.5-7 nm (DMPG), and this value remained almost unchanged for 40 days. These diffraction peaks completely vanished, when these dispersions were prepared above  $T^*$ . However, after incubation for more than 10 days, a repeat distance of the DMPG bilayer was recovered at 5.4-5 nm. On the other hand, the DSC measurements for the DMPG dispersions showed a large endothermic peak at  $T^*$  (31.7 °C). Such a peak would be caused by breaking of intermolecular and/or intramolecular hydrogen bondings formed with hydrophilic moieties. This configurational change in the polar moiety would trigger off progress of a high-order transition. When the dispersion had been incubated above  $T^*$ , a single sharp peak appeared around 45 °C after 15-20 days, which means appearance of new stable state.

### 391.D1 FROM SELF-ASSEMBLED, BILAYER LIPID MEMBRANES (BLMs) TO SUPPORTED BLMs ON METAL AND GEL SUBSTRATES TO PRACTICAL APPLICATION: An Overview

H. Ti Tien<sup>1</sup> and Angelica L. Ottova<sup>2</sup>

<sup>1</sup>Membrane Biophysics Lab (Giltner Hall), Department of Physiology, Michigan State University, East Lansing, Michigan 48824 (USA)

<sup>2</sup>Center for Interface Sciences, Department of Microelectronics, Slovak Technical University, Bratislava, Slovak Republic

Those whose work has no direct connection with biomembranes, perhaps are not acquainted with experimental lipid bilayers, commonly referred to as planar bilayer lipid membranes (BLMs) [1] and spherical liposomes [2]. These artificial systems have been extensively in the three decades as experimental models of cell membranes. The work began with D.O. Rudin and his associates in 1959-61. They first investigated lipid monolayers and multilayers of the Langmuir-Blodgett type, and then they toyed with soap bubbles and films. Upon realization that the structure of a soap film in air, in its final stage of tinning, has a structure which may be depicted as two lipid monolayers sandwiching an aqueous solution. That is a system which may be represented as *air/aqueous soap film/air*. Once they recognized this structure together with its molecular organization, Rudin and co-workers simply proceeded to make a under water "lipid film" separating two aqueous solutions, i.e., *aqueous solution/lipid bilayer/aqueous solution*. Experimentally, it is far easier to form a BLM than spreading a monolayer at an air/water interface. The accompanying table presents an historical overview of topics under discussion [3]. To impart relevant functions and specificity to BLMs, a variety of compounds such as ionophores, enzymes, receptors, photoactive dyes and pigments, fullerenes, etc. have been incorporated. Further, optical and electrical methods are readily applicable to such a planar BLM system. However, the conventional BLM system has one major limitation; it is not very stable for long-term studies and practical applications. This extreme fragility of the BLM has now been overcome. Simple methods are available for the formation of self-assembled, stable BLMs on either freshly cleaved metallic surface (s-BLMs) or freshly cut agar gel enclosed in a Teflon tubing (i.e., a salt bridge, hence sb-BLMs). Applications of these supported lipid bilayers can be envisaged, ranging from biosensors to molecular electronic devices. Finally, it should be stressed that such applications will require an interdisciplinary approach involving inputs from biophysics, colloid and surface science, and microelectronics.

Table 1. SELF-ASSEMBLING SYSTEMS (Taken from Ref. [3] where detailed citations may be found)

- |                                  |   |                |                    |
|----------------------------------|---|----------------|--------------------|
| 1. Soap films                    | 2. Monolayers                           | 3. Multilayers | 4. Bilayers (BLMs) |
| 5. Nucleopore Supported BLMs     | 6. Gold Supported Monolayers            |                |                    |
| 7. Metal Supported BLMs (s-BLMs) | 8. Salt-bridge Supported BLMs (sb-BLMs) |                |                    |

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### 392.D1 SELF-ASSEMBLY IN THE SYSTEMS BASED ON POLY(ETHYLENE-OXIDE) CONTAINING COMPOUNDS AND CYCLODEXTRINS

I.N. Topchieva, V.I. Gerasimov, I.G. Panova, K.I. Karezin, N.I. Ivanova,  
N.V. Efremova, S.V. Elezkaya

Department of Chemistry, Lomonosov State University, Moscow, Russia

The tendency of cyclodextrins (CD) to form inclusion complexes, "molecular necklaces", with poly(alkylene oxides) is well documented (1,2). These complexes comprise dozens of CD molecules threaded onto polymer chains. The stability of the complexes depends on the complementary between the internal cavity of CD and the thickness of the "guest" macromolecule. Thus, poly(ethylene oxide) (PEO) forms crystalline complex with six-membered  $\alpha$ -CD, whereas poly(propylene oxide) (PPO) - with seven-

membered  $\beta$ -CD. A step forward in this direction was made by using diverse PEO-containing compounds, namely, PEO-PPO block copolymers (Proxanols, Pluronic), linear and branched non-ionic detergents and star-shaped supermolecules (conjugates based on proteins and PEO). In this work much attention has been focused on complexes between PEO-PPO block copolymers (Proxanols, Pluronic) and CDs. These copolymers are nonionic amphiphilic polymers, in which PEO is a hydrophilic and PPO - hydrophobic parts of macromolecule. They are available as di- or triblock copolymers of diverse structures, molecular mass, and composition. Choosing  $\alpha$ - or  $\beta$ -CD as a host molecule, one can obtain complexes with PEO or PPO blocks of copolymers, correspondingly. These complexes depending on the type of copolymers may be either crystalline or watersoluble compounds. Crystalline complexes are characterized by the general composition, corresponding to one molecule of CD per two monomer units of poly(alkylene oxide). The crystallization of these compounds results in the formation of structures with hexagonal space-group. The cell dimensions indicate that  $\alpha$ -CD molecules treaded onto PFO-chains are stacked along the axis in a head-to-head fashion. These regularities are fulfilled if polymers are changed for nonionic detergents, e.g. Triton, Tween and so on. The complexation process may be easily recorded by measuring CMC values of detergents in the presence of CDs. The analysis of binding isotherms indicates the cooperativity of interaction and stoichiometry of complexes. It was found also that poly(alkylene oxides), covalently bound to the protein molecule, retain the ability to form insoluble inclusion complexes with CDs. Noticeable, that the stoichiometry of these complexes coincides closely with the stoichiometry in "molecular necklaces". All crystalline complexes based on PEO-containing compounds with diverse structure have the same structural motif, corresponding to the structure of molecular necklace.

### 393.D1 MESOPOROUS SILICA PATTERNS THROUGH TEMPLATED AND GUIDED GROWTH

M. Trau

*Department of Chemistry, University of Queensland, Brisbane Qld. 4072, Australia.*

Although self-assembled surfactant-silicate mesostructures have attracted much attention recently, their mechanism of formation has not yet been completely elucidated. Furthermore, although the formation of such structures as particles in solution is now a standard procedure, the construction of more complicated "designed" mesoporous structures has not yet been demonstrated. We have been investigating the formation and growth mechanisms of continuous mesoporous films and 1-dimensional structures on a variety of substrates<sup>1</sup>. In this paper we will demonstrate procedures for the formation and controlled growth of continuous mesoscopic surfactant-silica films of complex design. Films grown at the air/water, silica/water graphite/water and mica/water interfaces each display different morphological features depending on the nature of the surfactant-substrate interaction. As films grow away from the interface, random and chaotic structures ensue. To form oriented 1-dimensional structures, surfactant self-assembly and inorganic polymerization is carried out within the confined geometry of a patterned array of micro-capillaries. In-situ Atomic Force Microscopy and high resolution transmission electron microscopy have been used to reveal the detailed assembly mechanisms which operate in each case.

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### 394.D1 APPLICATION OF THE GERMAN FORMATION THEORY TO PHOSPHOLIPIDIC VESICLES.

A. O. Vila, C. Llacer, F. Molina, and J. Figueruelo

*Unidad de Investigación de Coloides. Dpt. de Química Física, Facultad de Farmacia, Universidad de Valencia. Avda, Vicent Andres Estelles s/n; 46100 Burjassot, Valencia, España*

The Theory of the new phase germen formation [1,2] has been applied to the formation of phospholipidic uni- and multilamellar vesicles. This new application starts from the Gibbs-Volmer's general laws for germen formation [3]. Surface energy, mechanical energy due to Laplace's overpressure and excess free energy (hydrophobic effect [4], chemical potential [5]) define the energetic barrier to be surmounted by



amphiphile molecules in order to form liposomes. Evaluation of those contributions as a function of vesicle size, of the lipid chemical nature and of bilayers number allows to define the experimental conditions at which vesicles should be formed. The Theory predicts spontaneous multilamellar liposomes formation of all phospholipid studied [6,7] according to experimental results in this field. Others outstanding consequences are also deduced.

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### 395.D1

#### SURFACE AGGREGATE PHASE TRANSITION

Erica J. Wanless\* and William A. Ducker

*Department of Chemistry, University of Otago, Dunedin, New Zealand.*

*\*current address: Department of Chemistry, University of Newcastle, Newcastle, Australia.*

Surface aggregate phase transitions are rare. Here we present a transition observed using Atomic Force Microscopy (AFM) at the graphite-solution interface in aqueous solutions of sodium dodecylsulfate (SDS) upon the addition of n-dodecanol. In pure SDS solutions, the surfactant aggregates on graphite into long hemicylindrical structures over the concentration range 2.8 to 81 mM<sup>1</sup>. Above the cmc of SDS, the addition of dodecanol causes no change to the surface structure, probably because of segregation of the dodecanol into the bulk micelles. Below the cmc, the addition of dodecanol results in a transition from the hemicylindrical surface aggregate morphology to a two-phase surface-aggregate structure consisting of a sheet structure coexisting with hemicylindrical structures. The lateral resolution of the AFM allows us to determine that the hemicylindrical structure is found preferentially at steps in the underlying graphite substrate. The first point defect in the hemicylindrical dodecylsulfate surface aggregate structure is also presented.

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### 396.D1

#### IRIDESCENT AND PHASE-SEPARATION PHENOMENA OF BILAYER MEMBRANES IN SURFACTANT GEL PHASE

Takamasa Yamamoto<sup>1</sup>, Naoki Satoh<sup>1</sup>, Tomohiro Onda<sup>2</sup> and Kaoru Tsujii<sup>1</sup>

<sup>1</sup>*Tokyo Research Center, Kao Corporation, 2-1-3 Bunka, Sumida-ku, Tokyo 131, Japan*

<sup>2</sup>*Recording and Imaging Science Laboratories, Kao Corporation, 2606 Akabane, Ichikaimachi, Haga-gun, Tochigi 321-34, Japan*

Iridescent phenomena of some kinds of surfactant and surfactant mixtures in dilute (1-2 wt%) aqueous solutions are one of the most interesting recent topics in the field of colloid and surface science<sup>1</sup>. The iridescent color appears by Bragg reflection of visible light from the periodic lamellar structure of bilayer membranes having a spacing distance of a sub-micrometer. Most of the iridescent surfactant systems reported so far are lamellar liquid-crystalline phase. The present paper deals with a novel iridescent system of surfactant gel phase being composed of a ternary mixture of triethanolammonium dihexadecylphosphate (DHP), water and ethanol<sup>2</sup>. It is particularly interesting to note in this system that the iridescent color can be changed with temperature (0 - 20°C), ethanol concentration (15 - 48 w%) and surfactant concentration (1.0 - 2.0 wt%) as well.

The structure of the iridescent gel phase has been studied mainly by small angle X-ray diffraction and ultraviolet and visible light reflection techniques, and determined to be a lamellar structure having the spacing distance of a sub-micrometer. So, color appearance of the solutions results from the same

mechanism as that of liquid crystalline phase. The iridescent color begins to shift to blue side at a certain critical temperature when temperature is elevated. Turbidity of the solution also starts to increase at the same critical temperature. When these critical temperatures are connected as a function of surfactant concentration, a curve similar to that of the LCST-type phase diagram is obtained. In the two-phase region of this diagram, their idescent color changes with temperature owing to the concentration change of the condensed (lamellar) phase, and does not change at constant temperature even when the surfactant concentration is altered. These novel phenomena in the present iridescent surfactant systems can be ascribed to the phase separation into a lamellar and a disordered bilayer structure of surfactant gel phase. This order-disorder phase transition is substantiated by the freeze-fracture electron microscopic technique.

Order-disorder phase separation phenomena in colloid dispersion systems have been known in mono-dispersed latices and other spherical colloidal systems<sup>3,4</sup>. Two kinds of theoretical explanation for this phase separation are still now in hot discussions. One is Alder transition theory<sup>3</sup> and the other is an electrostatic attractive interaction theory<sup>4</sup>. Our iridescent surfactant gel phase provides one more additional example of phase separation in the plate-shaped colloidal systems, and gives us a new challenging fundamental problem on the interactions between colloidal particles. Phase separation phenomena have never been observed in the iridescent lamellar liquid-crystalline phase. It is profoundly of interest why the phase separation occurs only in the system of solid bilayer dispersions (gel phase), and not in the liquid bilayer systems (liquid-crystalline phase).

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### 397.D1 SELF-ASSEMBLING IN POLYELECTROLYTE-SURFACTANT COMPLEXES: SPIN PROBE AND SPIN LABEL STUDIES

J.A.Zakharova<sup>1</sup>, V.A.Kasaikin<sup>1</sup>, A.M.Wasserman<sup>2</sup>, V.P.Timofeev<sup>2</sup>

<sup>1</sup>Department of Chemistry, Moscow State University, Moscow 119899, Russia

<sup>2</sup>Institute of Chemical Physics, Russian Academy of Science, Moscow 117334, Russia

Polyelectrolyte/surfactant complexes (PESC)s are a kind of self-organized, highly ordered systems. The influence of polyelectrolyte chain on the molecular mobility of surfactant ions in intramolecular micelles of PESC's, and the effect of surfactant binding on the conformational state of polyion have been investigated by spin probe and spin label techniques. Complexes of poly(acrylic acid), or poly(methacrylic acid) (PMA) with alkyltrimethylammonium bromides were studied. The spin probe was insoluble in water but was solubilized by surfactant micelles or intramolecule micelles of PESC's. Thus, the spin probe rotation correlation time ( $\tau$ ) represented the molecular mobility of surfactant ions in the micelles. It was found that  $\tau$  value in PESC's was higher than that in free micelles. It means that Coulombic association of surfactant ions with oppositely charged polyelectrolyte chains led to decrease of the molecular mobility of surfactant ions. The composition of PESC's does not influence the molecular mobility of surfactant ions. Moreover, the phase transition caused by formation of insoluble stoichiometric PESC's also does not effect the spin probe molecular mobility. Thus, the structure of internal micelles of PESC's remained unchanged at different complex composition and phase state, the molecular mobility of surfactant ions in PESC's being much more lower than in free micelles.

Analysis of ESR-spectra of spin-labeled PMA indicated that at pH=6 the spectrum is a combination of the two spectrum, attributed to fast and slow rotation of the label. Mathematical simulation of experimentally observed spectrum led us to the conclusion that at pH=6, compact "ternary" structure of PMA chains partly retained. Increase of pH from 6 to 9 causes additional ionization of PMA, and the breaking down of hydrogen bonds between unionized groups of PMA. This resulted in the complete distraction of the compact conformational state of PMA and increase of segmental mobility of polymer units. At pH=6, complex formation induced the breaking down of the compact conformation of PMA when surfactant concentration increased. As a result, ESR-spectrum of PESC became identical to spectrum of PMA at pH=9.

Besides, at pH=9 complex formation does not influence ESR spectra at all. The values of isotropic hyperfine splitting constants indicate water environment of the label in PESCs.

Based on the data obtained, the schematical structure of PESCs was proposed. These complexes may be regarded as asymmetrical species in which polymer chains occupied the exterior parts of the micelles. Importantly, the initial conformation of PMA retained when PESCs were formed. This model takes into account the hydrophobic interactions between surfactant alkyl radicals and meet the minimum entropy stress of polymer chain.

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## 398.D2

### THE DIMMER OF IN AQUEOUS SOLUTION SODIUM N-OCTYLE BENZENE SULPHONATE

V.I. Ananchenkov, R.M. Galimzyanov, A.A. Saidov, K.N. Kholov

*Heat physics department AS Uzbek Republic, Tashkent.*

The space aspects of sodium n-octyle benzene sulphonate ( $\text{OBS} = \text{Na-SO}_3\text{-C}_6\text{H}_4\text{--}7(\text{CH}_2)\text{-CH}_3$ ; the group  $-7(\text{CH}_2)\text{-CH}_3$  is in conformation state trans-trans- ...-trans) molecules association in aqueous solution have been considered by means of the methods [1,2]. In Decart space XYZ, reflecting the position of second molecules of dimer relatively to the first molecule, located in the beginning of coordinate, the grid of global minima of total energy is constructed. For intermediate states the hydrophobic component of total energy approximated on value of its Van der Waals components. The global minima in each space points are found by method of mobile borders of conformational domains, which is determined by parameter - threshold of conformation deference. The spacious discrete nature of domains connected with power-generating minima, possessing final conformational change on dividing them border is shown. The defect of energy in dimerization process is  $\Delta E - 8$  kkal/mol, at  $20^\circ\text{C}$   $\langle \Delta E \rangle - 4$  kkal/mol. The Van der Waals and hydrophobic interactions have approximately almost equal values. This may be interpreted as an argument for dominating of the OBS dimers over their monomers in aqueous solution at room temperatures.

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## 399.D2

### THE NATURE OF THE HEXAGONAL- MICELLAR PHASE TRANSITION IN AN AQUEOUS SOLUTION OF $\text{C}_{10}\text{H}_{21}(\text{OCH}_2\text{CH}_2)_5\text{OH}$

Nicolai Goutev, Zhorro S. Nickolov

*Department of Quantum Electronics, Faculty of Physics, Sofia University,  
5, J Bouchier Bul, 1164 Sofia, Bulgaria*

The nature of the transitions between isotropic - anisotropic phases in the system polyoxyethylene surfactant/water is an interesting problem which is not fully understood. Recent investigations of the characteristics of water in the system  $\text{C}_{10}\text{E}_5$ /water by Raman and depolarized Rayleigh-wing scattering [1] showed that the hydrogen bonded structure of water changes abruptly at the transition micellar( $L_1$ ) - hexagonal( $H_1$ ) phase. It is intriguing to investigate how does the structure of the amphiphile change at this transition. In the present work the regions of the skeletal vibrations,  $\text{CH}_2$ -deformation vibrations and C-H stretching vibrations of the surfactant have been analysed close to the transition hexagonal( $H_1$ ) - micellar( $L_1$ ) phase by Raman scattering. These regions reflect eventual changes in the structure of micelles.

It is well known that the phase transitions in aqueous surfactant solutions originate from changes in the intramicellar and intermicellar interactions. We have compared the observed changes in the Raman bands of the surfactant molecules and in the OH stretching band of water using difference spectra. The results from our study show that the changes in the surfactant bands are very small and continuous at the transition and therefore there are no significant intramicellar changes at the phase transition. On the contrary, the changes

in the water OH band are well expressed, demonstrating a stepwise increase in the coordination of the water molecules in the hexagonal phase. From these facts we can suggest that the transition  $H_1-L_1$  studied here is mainly due to changes in the hydrogen bonded structure of water between the micelles and that the intramicellar changes have a minor effect. Thus we can assume that the hexagonal( $H_1$ ) - micellar( $L_1$ ) phase transition in  $C_{10}E_5$ /water is driven by intermicellar interaction in which the hydrogen bonded structure of water plays a very important role.

We propose the following mechanism of the studied transition. Water molecules close to hydrophilic surfaces (for example the surfaces of the micelles in our case) are better structured than those in bulk water. In the micellar phase the layer of structured water around the micelles will induce a short range repulsive hydration force between them [2]. The thickness of the hydration layer should increase with decreasing temperature. At a particular temperature (the temperature of the phase transition) the effective radii of the micelles become too large and the mesophase is formed due to the limited ability of the micelles to move freely in the system. The water molecules between the micelles in the hexagonal phase are connected in a common more organised network - the structure of water can be considered as highly tetraordinated in respect to the water in the micellar phase.

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## 400.D2      STRUCTURAL STABILITY AND MOLECULAR IMAGING OF DEFECT-DIMINISHED FATTY ACID MONOLAYERS

Tisato Kajiyama and Taishi Kuri  
*Kyushu University, Fukuoka, Japan*

The aggregation structure of fatty acid monolayers on the water surface have been classified with respect to thermal (the sub-phase temperature:  $T_{sp}$ , the crystalline relaxation temperature:  $T_{\alpha c}$ , the melting temperature:  $T_m$ ) and chemical (the degree of ionic dissociation of hydrophilic group) factors. In the case of amphiphiles with a non-ionic hydrophilic group, the monolayers are formed in the states of "the amorphous monolayer", "the randomly assembled crystalline monolayer" and "the fusing-oriented crystalline monolayer" for the conditions of  $T_m < T_{sp}$ ,  $T_{\alpha c} < T_{sp} < T_m$  and  $T_{sp} < T_{\alpha c} < T_m$ , respectively.

Based on the new concept of monolayer classification mentioned above, the several monolayer preparation methods have been proposed to obtain the defect-diminished monolayers of fatty acids. The monolayer prepared by a multistep creep method was morphologically homogeneous even after the area-creep at a high surface pressure where the monolayer prepared by a continuous compression method was collapsed. The monolayer prepared by a multistep creep method was mechanically stable because of the reduction of the stress concentration in the monolayer by the structural relaxation during the multistep creep process. Therefore, the multistep creep method is useful for the construction of the defect-diminished and mechanically stable monolayer.

Molecular-resolution images of fatty acid molecules in the monolayers on mica substrate were successfully observed with an atomic force microscope (AFM). The AFM image of a lignoceric acid monolayer prepared by at a surface pressure of  $5 \text{ mN m}^{-1}$  showed a two-dimensional periodic locally structure with disordered molecular arrangements. Also, the nondestructive AFM image observation was successful for a stearic acid monolayer which was prepared by a multistep creep method, indicating that a high mechanical stability of the monolayer is inevitably required for the nondestructive AFM observation.

## 401.D2      AN UNEXPECTED MECHANISM FOR FORMATION OF DYE-POLYELECTROLYTE MULTILAYERS

Matthew R. Linford, Helmuth Möhwald, Mark Auch  
*Max-Planck-Institut für Kolloid- und Grenzflächenforschung, D012489, Germany*

We have observed an unexpected mechanism in the formation of multilayers of polyelectrolyte polymers and multiply-charged organic dyes. When the polymer-coated substrate is put into a solution with

an oppositely-charged dye, the dye adsorbs into the polymer. When the polymer-dye surface is reimmersed into the original polymer solution, a fraction (up to 100%) of the dye may be extracted by the polymer solution. This extraction takes place at intermediate salt concentrations while at very high or very low ionic strength less extraction or in some cases even no extraction is observed. At low salt concentration, the polymer's persistence length should be high. These conditions have been shown in the literature to be unfavorable for complexation between polyelectrolyte polymers and dyes. High salt concentrations reduce the polymers persistence length and also collapse the double layers surrounding both the polymer and the dye-coated surface so as to favor polymer adsorption (and not dye extraction). We discuss here the different results obtained by varying the salt concentration in preparation of multilayers of polystyrene sulfonate/ingrain blue 1 (a copper phthalocyanine dye with four positive charges), polyallylamine hydrochloride/direct blue 71 (an azo dye with four negative charges), and diallyldimethylammonium chloride/direct blue 71.

## 402.D2

### THE TWO-DIMENSIONAL STRUCTURE OF THIOLS AND DISULFIDES ON GOLD(111)

G. Nelles<sup>1</sup>, H. Schönherr<sup>2</sup>, M. Jaschke<sup>4</sup>, H. Wolf<sup>2</sup>, M. Schaub<sup>3</sup>, E. Bamberg<sup>4</sup>,  
H. Ringsdorf<sup>2</sup>, H.-J. Butt<sup>1</sup>

<sup>1</sup>*Institut für Physikalische Chemie,*

<sup>2</sup>*Institut für Organische Chemie, Universität Mainz, 55099 Mainz, Germany*

<sup>3</sup>*Dept. of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139*

<sup>4</sup>*Max-Planck-Institut für Biophysik, Kennedyallee 70, 60596 Frankfurt, Germany*

Thiols and disulfides form spontaneously monolayers on gold. In order to find factors which determine their two-dimensional packing several classes of thiols and disulfides on gold(III) have been imaged by atomic force microscopy. Monolayers were formed from different n-alkanethiols, fluorinated and normal(alkanoat)-ethyl disulfides, different azobenzenethiols and disulfides, diacetylene disulfides and anthracene terminated thiols and disulfides. All images were taken in ethanol to be able to reduce the force down to 0.1 nN and to image at highest possible resolution. In all cases two-dimensional crystals could be clearly resolved. The lattices were quantitatively analyzed.

A simple picture of the two-dimensional packing of thiols on gold emerged: All thiols and disulfides seem to form either a hexagonal or a distinctly different centred rectangular lattice. Hexagonal lattices were formed by long thiols with a relatively spherical cross-section. Centred rectangular lattices were formed by thiols with an asymmetric cross-section.

The transition between the two structures could be observed with the (alkanoat)ethyl disulfides  $[\text{CH}_3(\text{CH}_2)_n\text{COO}(\text{CH}_2)_2\text{S}]_2$ ,  $n = 6, 8, 10, 12, 15, 16$ . Disulfides with long alkyl chains ( $n > 12$ ) formed hexagonal lattices. For disulfides with short alkylchains, where asymmetry imposed by the ester group dominates, not only domains with a hexagonal lattice but also centred rectangular domains were observed in parallel. The length of the alkyl chain determined the probability of finding disulfides in the hexagonal structure rather then changing the structure itself.

In addition, by investigating (alkanoat)ethyl disulfides with different chain lengths we found that the tip of the atomic force microscope probably penetrates more the 5 Å into the monolayer.

## 403.D2

### DIFFUSION OF BOUND WATER ALONG MACROMOLECULE SURFACE: A SIMPLE MODEL FOR DIFFERENT DNA CONFORMATIONS

M.Ye. Tolstorukov<sup>1</sup>, K.M. Virnik<sup>2</sup>, V.Ya. Maleev<sup>1</sup>

<sup>1</sup>*Kharkov State University, Kharkov, Ukraine*

<sup>2</sup>*Institute of Radiophysics and Electronics, Nat. Acad. of Sci. of Ukraine, Kharkov, Ukraine*

One of the main factors defining the structure and physical properties of the DNA molecule is its ion-hydrate surroundings. The conformational state of the DNA molecule is in the strong dependence on the water contents and concentration and type of the counterions. In connection with that it is interesting to study

physical properties of the interaction of the ion-hydrate surroundings with DNA molecule. One of the base characteristics of that interaction is the water diffusion coefficient near the DNA molecule surface.

We carried out estimation of water diffusion coefficient in the hydrate surroundings of an individual of an individual DNA molecule for different DNA conformations with various water contents.

A simple model is proposed to describe water diffusion process. The water molecules was assumed to diffuse according to Fick's law; a DNA molecule matrix was considered as lattice structure. As DNA molecule is known to have very complicated structure of the surface, it was assumed that the DNA sorbing surface has a fractal dimension. The fractal dimensions of the A- and B-forms of the DNA molecules was estimated by using methods of the determination of the accessible surface areas. The fractal dimensions of the DNA molecule according to our calculations are 3.01 for A-form and 2.46 for B-form of DNA. These values are defined with DNA conformations and, therefore, fractal dimensions can be considered as a characteristic of the DNA secondary structure. The value of the A-DNA fractal dimension is greater than that of B-DNA and this fact is in agreement with crystallographic data according to which A-DNA is more closely packed than B-DNA.

The diffusion coefficients of bound water molecules was calculated within each interval of relative humidity where DNA molecule restores its conformation. They monotonically increase what is in connection with decrease of the mean relaxation time of bound water molecules, which, in its turn, is defined with increase of the water molecule indirectly bound to the DNA binding sites. The value of the water diffusion coefficient for high values of the relative humidity is approximately equal to one for a bulk water.

Water diffusion of the type considered probably could contribute to the local conformational changes of the DNA molecule.

## 404.D2 THE PHASE BEHAVIOUR OF A MIXED LYOTROPIC SYSTEM

A. Zheliaskova and A. Derzhanski

*Institute of Solid State Physics, BG-1784 Sofia, Bulgaria*

The binary systems (lecithin-water) and (triton-water) are characterized by a steady lamellar phase in a large concentration interval at room temperature.

In the present study the phase behaviour of the ternary system lecithin-triton - water was investigated by means of NMR method. The lyotropic phases were identified from the  $^{31}\text{P}$  and  $^2\text{H}$  absorption NMR spectra.

The shape of the resulting spectra gives allows us to divide the samples into three groups: (A) samples with considerably higher content of lecithin compared to that of triton; (B) samples with approximately equal contents of lecithin and triton, and (C) samples with a relatively lower content of lecithin. The samples of group B exhibit spectra with two peaks. We presume these peaks correspond to two coexisting lamellar phases. Moreover, we consider the occurrence of two subsystems - one containing predominately lecithin with triton as an admixture and another with prevailing content of triton having the lecithin as an admixture. The lecithin molecules occur in both subgroups with different probabilities. Their phosphorus atoms are situated in non-equivalent conditions from the point of view, of the NMR method. They have different absorption lines every one with its own amplitude and shift in the main spectrum. The absence of a common absorption spectrum shows that the two mesogens (lecithin and triton) do not mix in a homogeneous system. This is due to their different structures: lecithin molecules possess a relatively large hydrocarbon part and relatively small bulk hydrophilic head whilst in triton molecules one observes just the opposite picture - long hydrophilic part and considerably smaller bulk hydrophobic one. The spectra of group A resemble the ones of the binary system (lecithin-water). A single lamellar phase appears; the relatively small amount of triton does not stimulate the formation of a second phase, but stabilizes the existing lamellar phase in a more expanded interval. In group C similarly only one lamellar phase occurs. At a low water content an isotropic phase is also observed. The behaviour of group C's samples resembles the binary system triton-water. The admixture of lecithin broadens and stabilizes the lamellar phase.

**405.D3**

**SURFACE TENSION KINETICS OF  
DIMYRISTOYLPHOSPHATIDYLCHOLINE VESICLES AT AIR/WATER INTERFACE  
BELOW AND ABOVE THE MAIN PHASE-TRANSITION TEMPERATURE**

**L. Alexandrova<sup>1</sup>, B. Tenchov<sup>1</sup> and L. Grigorov<sup>2</sup>**

*<sup>1</sup>Institute of Biophysics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

*<sup>2</sup>Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

The surface tension kinetics of aqueous suspensions of small unilamellar dimyristoylphosphatidylcholine (DMPC) vesicles at air/water interface has been studied by the Wilhelmy plate method. The experiments were performed at different concentration at two temperatures, 20 and 30 °C, below and above the main-phase transition temperature of the used lipid.

Marked changes in both the kinetics constant and ultimate surface tension characterize the concentration and temperature dependence of surface tension kinetics of DMPC. The kinetic model based on the assumption of irreversible adsorption process is proposed.

**406.D3**

**EFFECT OF TEMPERATURE ON KINETICS OF AIR/VESICLE  
SUSPENSION/QUARTZ THREE-PHASE CONTACT**

**L. Alexandrova<sup>1</sup>, R. Tzekov<sup>2</sup>, R. Koynova<sup>1</sup> and L. Grigorov<sup>2</sup>**

*<sup>1</sup>Institute of Biophysics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

*<sup>2</sup>Department of Chemistry, University of Sofia, 1164 Sofia, Bulgaria*

The stability of wetting films on quartz surface from suspensions of multilamellar dimyristoylphosphatidylcholine (DMPC) vesicles are studied between 20 (below) and 35 °C (above the phase-transition temperature) by measurement of the film lifetime  $\tau$  and the three-phase contact kinetics. It has been found that  $\tau$  has a minimum as a function of temperature while the dynamic contact angle reaches a maximum there. The obtained results were explained by the existence of hydrophobic attraction force between the film surfaces. The model for the film rupture is proposed.

**407.D3**

**PRECISION OF MEASUREMENTS OF THERMAL SHAPE  
FLUCTUATIONS OF QUASI SPHERICAL LIPID VESICLES. RELATION  
TO CORRELATION BETWEEN FLUCTUATION MODES**

**I. Bivas<sup>1,2</sup>**

*<sup>1</sup>French-Bulgarian Laboratory "Vesicles and Membranes" supported by the CNRS France  
and the Bulgarian Academy of Sciences, Bulgaria*

*<sup>2</sup>Institute of Solid State Physics, Bulgarian Academy of Sciences, Laboratory of Liquid Crystals,  
72 Tzarigradsko Chaussee Blvd., Sofia 1784, Bulgaria*

The measurement of the thermal shape fluctuations of quasispherical vesicles is one of the experimental methods for assessment of the bending elasticity of their lipid bilayers. For this aim, the fluctuations are expanded in a series of spherical harmonics. The amplitudes of the obtained space modes are time dependent. There exist theories expressing the mean square amplitudes of each of the modes by the bending elasticity of the membrane and by either its tension [1] or its excess area [2].

When a vesicle is observed under a microscope, usually its maximal cross-section perpendicular to the optical axis (the so called equatorial cross-section) is visualized, and not its whole membrane. It is possible to link up the bending elasticity of the bilayer to the shape fluctuations of the vesicle's quasi circular equatorial cross-section, expressing them by the space modes of fluctuation [3].

In the present work, the standard deviation is calculated of the experimentally measured quantities related, to the fluctuations of the equatorial cross section of the vesicle. Results are obtained for the cases of not correlated [1] and correlated [2] fluctuation space modes. For the treatment of the second case, all

appropriate Monte-Carlo simulation of the shape fluctuations of the vesicle was accomplished. The numerical results for the two cases are not substantially different.

Our results will permit the precision of the calculated bending elasticity modules of the lipid bilayer to be improved and the limits of application of the used experimental procedure to be outlined.

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### 408.D3 DYNAMICS OF THERMAL SHAPE FLUCTUATIONS OF FLACCID QUASI SPHERICAL LIPID VESICLE WHEN INTERMONOLAYER FRICTION IN ITS BILAYER IS TAKEN INTO ACCOUNT

I. Bivas<sup>1,2</sup>, P. Méléard<sup>1,3</sup>, I. Mircheva<sup>1,2</sup>, P. Bothorel<sup>1,3</sup>

<sup>1</sup>*French-Bulgarian Laboratory "Vesicles and Membranes" supported by the CNRS France and the Bulgarian Academy of Sciences, Bulgaria*

<sup>2</sup>*Institute of Solid State Physics, Bulgarian Academy of Sciences, Laboratory of Liquid Crystals, 72 Tzarigradsko Chaussee Blvd., Sofia 1784, Bulgaria*

<sup>3</sup>*Centre de Recherche Paul Pascal, CNRS, Av. du Dr. Albert Schweitzer, F-33600, Pessac, France*

In the previous theories dealing with shape thermal fluctuations of quasi spherical vesicles [1, 2], the membrane was considered as a homogeneous shell characterized by its bending modules. Our description considers the fluctuations to be followed by a lateral redistribution of the molecules within the bilayer limited by an intermonolayer friction. These phenomena keep the expressions for the mean square values of the fluctuation mode amplitudes [2], but change the theory of their dynamic behavior. The corrections to the previous theory [2] are expressed through the bending moduli  $k_c^{bl}$  and  $k_c^{fr}$  characterizing respectively a blocked and free exchange of the molecules within the monolayers [4], and by the friction coefficient between the monolayers. Numerical estimations show that effects have to be observed when shape fluctuations of giant quasi spherical vesicles ( $\sim 10\mu\text{m}$ ) are analyzed.

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### 409.D3 INFLUENCE OF CONCENTRATION AND POLYMER CHAIN LENGTH OF MODIFIED LIPID ON THE ELASTIC PROPERTIES OF LIPID LAYER

I. Bivas<sup>1,2</sup>, M. Winterhalter<sup>3</sup>, M.D. Mitov<sup>1,2</sup>, P. Méléard<sup>1,4</sup>, P. Bothorel<sup>1,4</sup>

<sup>1</sup>*French-Bulgarian Laboratory "Vesicles and Membranes" supported by the CNRS France and the Bulgarian Academy of Sciences, Bulgaria*

<sup>2</sup>*Institute of Solid State Physics, Bulgarian Academy of Sciences, Laboratory of Liquid Crystals, 72 Tzarigradsko Chaussee Blvd., Sofia 1784, Bulgaria*

<sup>3</sup>*Biozentrum, Biophys. Chemie, Klingelbergstr. 70, Ch-4056 Basel, Switzerland*

<sup>4</sup>*Centre de Recherche Paul Pascal, CNRS, Av. du Dr. Albert Schweitzer., F-33600 Pessac, France*

The inclusion of lipids with covalently bonded polymers (polyethylene glycol, PEG) in the membranes of the liposomes is used to improve the liposome circulation time in the blood [1]. The presence of modified lipids changes the elastic properties of the lipid bilayer. The aim of the present study is to measure the dependence of the bending elasticity of a lipid bilayer and the stretching elasticity of a lipid monolayer on the concentration of the contained in them modified lipid and on the length of its polymer chain. The method chosen for measuring the bending elasticity is the micropipette technique (for details, see [2]). It consists in sucking a vesicle into a glass capillary with a diameter smaller than the vesicle one. The bending modules is deduced from the dependence between the aspiration pressure and the length of the



vesicle membrane aspired into the micropipette, when the pressure is small enough. The stretching elasticity of the monolayer is measured by classical Langmuir trough.

Recently, a theory was proposed for the influence of the modified lipids on the elastic properties of the lipid bilayers and preliminary experiments were performed for the dependence of the bending elasticity of a SOPC bilayer on the concentration of PEG-lipid with molecular weight of the polymer chain MW=2000 [3]. The new experimental results would permit to verify the theory and to estimate the structural parameters (length of the monomer unit and persistent length) of the polymer chain of the modified lipid.

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## 410.D3 A CUBIC PHASE OF DENSELY PACKED MONODISPERSE, UNILAMELLAR VESICLES

**H. Hoffmann, M. Gradzielski, M. Müller, M. Bergmeier**

*Lehrstuhl für Physikalische Chemie I, Universität Bayreuth, D - 95440 Bayreuth, Germany*

A novel type of gel phase has been investigated in the ternary surfactant system sodiumoleate/octanol /water. It occurs at a relatively high octanol content, i. e. at a molar ratio of ~ 2:1 for octanol/ oleate where the total concentration of amphiphile is in the range of 5 - 15 wt %. This phase is transparent, isotropic, highly viscous and possesses elastic properties ("ringing gel"). Microstructural investigations by means of freeze-fracture electron microscopy and small-angle neutron scattering show that is mainly composed of small uni-lamellar vesicles. The observed size is also in good agreement with the measured rheological properties. These vesicles are remarkably monodisperse and form a highly ordered phase (presumably of a cubic type), i. e. this is the first time that such a liquid crystalline array of vesicles has been observed. This finding might have some potential for applications in biophysics, pharmaceutical preparations, etc., where exactly such properties, i. e. very well-defined sizes of vesicles and a highly ordered structure, are required.

## 411.D3 POLYMERIZATION IN VESICLES: A KINETIC STUDY USING PULSED LASER POLYMERIZATION

**Martin Jung, Alex M. van Herk, Anton L. German**

*Laboratory of Polymer Chemistry, Eindhoven University of Technology, P.O. Box 513,  
5600 MB Eindhoven, The Netherlands*

The poor colloidal stability of vesicles has always been an obstacle on the way to applications. The resulting need for stabilisation led to the application of polymerizable surfactants. Subsequently, polymerized surfactant vesicles have become the most sophisticated systems in the armory of membrane mimetic chemists. A great variety of polymerizable surfactant molecules have been synthesised and their potential is largely investigated. Another route of stabilisation has been suggested by Murtagh and Thomas<sup>1</sup>. They proposed to swell the lipophilic bilayer of the vesicle with monomer and polymerize then the monomer within the surfactant bilayer. Henceforth, a new type of polymerization in heterogeneous media was added to the canon of the classical systems (emulsions, microemulsions etc.).

In short, the process of polymerization in vesicles can be subdivided in three essential steps: (1) preparation of vesicles, (2) swelling of the bilayer with monomer, (3) free radical polymerization of the monomer.

Towards a kinetic understanding of the polymerization process in vesicles we performed a Pulsed Laser Polymerization (PLP) study to gain information about basic system parameters, e.g. *the monomer concentration at the site of reaction*.

As model system we used Dioctadecyldimethylammoniumbromide as a vesicle forming surfactant and styrene as monomer.

In heterogeneous systems, the monomer concentration at the site of reaction differs from the *overall* monomer concentration as a consequence of partitioning. For the description of kinetics in heterogeneous systems, this local concentration is of great importance. One method to determine *directly* the concentration of monomer at the site of polymerization is the PLP/SEC method. Here, the growing time of a single polymer chain equals the time between two laser pulses. From an analysis of the resulting molecular weight distribution, determined by means of size exclusion chromatography, the monomer concentration can be derived.

The application of PLP experiments to determine the monomer concentrations in other heterogeneous systems like microemulsions and latices<sup>2</sup> has proved to be successful. Here, we report the results of a PLP study in vesicular structures to determine the *concentration of a solute (monomer) in a bilayer* - a parameter which is to our knowledge by no other means accessible and has never been determined experimentally before. In addition to the thermodynamic data of the solute concentration in surfactant bilayers we discuss the kinetic insights from the pulsed laser study in this special heterogeneous system.

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## 412.D3

### CHARACTERISATION OF CATIONIC VESICLES BY MICROSCOPY AND NMR SELF-DIFFUSION

Eduardo Marques<sup>1,2</sup>, Oren Regev<sup>3</sup> and Ali Khan<sup>2</sup>

<sup>1</sup>Physical Chemistry 1, Lund University, Lund, Sweden

<sup>2</sup>Department of Chemistry, University of Coimbra, Coimbra, Portugal

<sup>3</sup>Department of Chemical Engineering, Ben-Gurion University, Beer-Sheva, Israel

Cationic mixtures are aqueous mixtures of oppositely charged surfactants which display novel bulk and interfacial properties in comparison with the parent surfactants. One bulk property is the ability of these systems to spontaneously form highly stable vesicles at low concentrations. The phase behaviour of the mixture sodium dodecyl sulphate (SDS) - didodecyl dimethyl ammonium bromide (DDAB) has been studied in detail and two regions of isotropic vesicular phases (anionic-rich and cationic-rich) are identified.

Cryo transmission electron microscopy allows direct visualisation of relatively polydisperse small unilamellar vesicles for the SDS-rich side and large unilamellar vesicles for the DDAB-rich side. It also provides the microstructure evolution from mixed micelles to vesicles as the surfactant mixing ratio is changed towards equimolar solid formation. The <sup>1</sup>H NMR FT pulsed gradient spin echo technique is used for the measurement of solvent and surfactant self diffusion coefficients. Water molecules can be in fast or slow exchange between the inside and outside of the vesicle within the experimental time scale (the variable parameter  $\Delta$ ), depending on membrane permeability and vesicle size. In the case of fast exchange only one average coefficient is obtained, but for slow exchange a biexponential decay is usually observed. For the SDS-rich vesicles, the persistence of a low fraction slow component for the echo decays, even for large values of  $\Delta$ , indicates the presence of very large vesicles coexisting with the smaller ones. Optical microscopy confirms the presence of vesicles of several microns of diameter. Thus, high polydispersity is an inherent feature of this system, as revealed both by cryo-TEM and NMR self-diffusion as complementary techniques. Surfactant diffusion measurements provides further information on the coexistence of surfactant aggregates and estimation of sizes.

An area of considerable interest is also that of interactions between surfactant vesicles and polymers, namely phenomena such as gel formation. Recent microscopy studies on mixtures of SDS/DDAB vesicles and polymers are presented.

## 413.D3

EFFECT OF SURFACE MOBILITY ON FOAM LIPID  
(DPPC) FILMS EVOLUTION

D.J. Mitev, R. Tsekov, C.S. Vassilieff

*Department of Physical Chemistry, Faculty of Chemistry, University of Sofia, Bulgaria*

The kinetic behaviour of aqueous foam films containing unilamellar DPPC (dipalmitoyl-phosphatidyl-choline) vesicles is studied making use of the microinterferometric method of Scheludko and Exerowa. Symmetric dimple evolution is registered with different lipid concentrations (0,1-0,8g/l). The dimple flat-tening is parameterized in a simple way:

- the axisymmetric dimple shape is described with a polynomial where three coefficients have a clear physical meaning;
- the dimple half-height in the film centre (one of the polynomial coefficients) diminishes exponentially with time.

The dimple flattening is described theoretically solving numerically the hydrodynamic equations using surface mass and force balances as boundary conditions. The gradient of the surface tension, determined by interfacial lipid mass transfer kinetics (vesicles desintegration), governs the tangential surface mobility.

The comparison between calculated and experimental results proves the tangential mobility of the film surfaces. The data are used to estimate the rate constant of lipid release from metastable surface aggregates. The values are in order of magnitude coincidence with previous estimates from plane-parallel film thinning kinetics.

## 414.D3

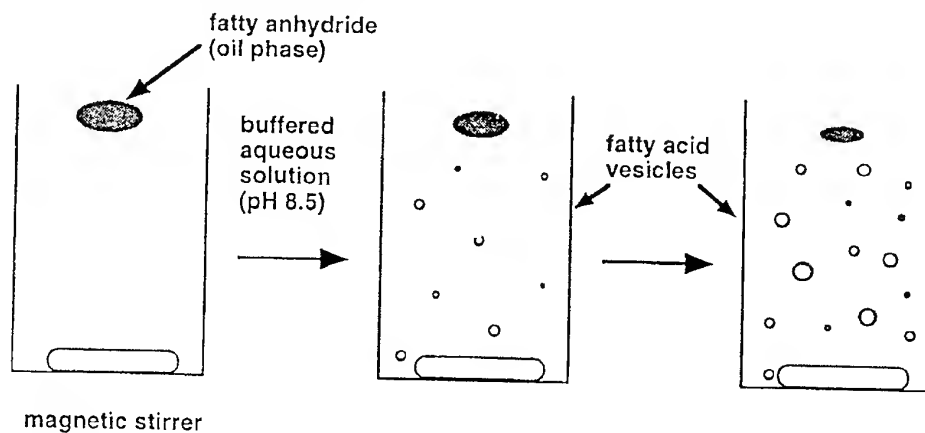
## SELF-REPRODUCTION OF FATTY ACID VESICLES

K. Morigaki, M. Blocher, P. Walde, P.L. Luisi

*Institut für Polymere, ETH-7, Universitätstrasse 6, CH-8092, Zürich, Switzerland*

In the context of the origin of life and prebiotic cell models, we are currently investigating experimental possibilities of the self-reproduction of vesicles. Self-reproduction is one of the key processes in living structures and one which is supposed to have played a fundamental role during the prebiotic events which led to the transformation of the non-living to the living.

We have studied the self-reproduction of vesicles which are composed of fatty acid molecules under conditions where about half of the fatty acid molecules within the vesicle bilayer are deprotonated (1). The vesicles are first formed due to a simple chemical reaction: the hydrolysis of water-insoluble fatty anhydride leads to the formation of two molecules of fatty acids which spontaneously assemble into vesicles. As soon as the vesicles are formed, the hydrolysis of the anhydride is accelerated, leading to an increase in the number of vesicles as time progresses. This autocatalytic vesicle self-reproduction process schematically illustrated below has been investigated under different experimental conditions (chemical structure of the fatty acids/ anhydrides, pH, buffer ions, temperature) in order to get a deeper insight into the mechanism of the reproduction process. The newest results will be presented.



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## 415.D3 REORGANISATION & BLISTERFORMATION IN CONTACT AREA OF ELECTROSTATICALLY ADHERING VESICLES

J. Nardi<sup>1</sup>, R. Bruinsma<sup>2</sup>, E. Sackmann<sup>1</sup>

<sup>1</sup>TU München, Physik Department (E22), 85747 Garching, Germany

<sup>2</sup>UCLA, Chemistry Department, USA

The electrostatic adhesion of positively charged giant vesicles on negatively chargeable supported membranes is controlled by triggering the surface charge density of the supported membrane via volume pH in a specially designed dialysis chamber.

In order to ensure quantitative studies, microinterferometry (RICM) and Laserscanning Microscopy (LSM) are used. RICM allows quantitative evaluation of contact formation and surface profile near contact area. By using LSM the complete three dimensional shape of the adhering vesicle can be continuously studied.

When increasing the surface charge density of the supported membrane beyond a threshold value, in contact area the vesicle membrane shows areas of close contact and blisters of higher distance to the supported membrane.

For explaining this phenomenon, a theory was developed. It treats the statics and dynamics of the adhesion between fluid membranes with charges of opposite sign.

Comparison of the experimental data with theoretical predictions show, that (1) different charge densities of the two interacting membranes are necessary, (2) the basic process for blistering is a lateral reorganisation of the charged lipids in the less charged membrane into area with high and areas with low amount of charged lipids, (3) a critical charge density is required to start the blister formation, (4) this critical value is independent of the amount of charged lipids, (4) the solutes in the water are collected in the blisters, which pressures them.

The important and biologically relevant aspect of this phenomena is, that in contact area the compositions of membranes consisting of different types of lipids can be locally varied. This reorganisation can cause itself a lateral redistribution of functional units as receptors, channels or various signalling molecules. Therefore this phenomena is a further hint, that simple mechanisms may be the key to how nature organises its complexity.

## 416.D3 EFFECT OF GRAFTED PEG-2000 ON THE SIZE AND PERMEABILITY OF VESICLES

A. Nikolova<sup>1</sup> and M. N. Jones<sup>2</sup>

<sup>1</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

<sup>2</sup>School of Biological Sciences, University of Manchester, Manchester M13 9PT, UK

The permeability of PEG - derivatized vesicles produced by the extrusion technique (VETs) to encapsulated D-glucose has been studied. Vesicles were prepared from mixtures of dipalmitoylphosphatidylcholine (DPPC), phosphatidylinositol (PI) and dipalmitoylphosphatidyl-ethanolamine with covalently attached poly-(ethylene glycol) of molecular weight 2000 (DPPE-PEG2000). The occurrence of an irreversible temperature-induced size transition of the PEG-derivatised VETs was detected close to the temperature of the main phase transition of the predominant phospholipid component by photon correlation spectroscopy. The permeability of the vesicles towards radioactive D-glucose was studied by a method similar to the one proposed by Johnson and Bangham at 25, 37 and 50 °C for VETs with DPPE-PEG content from 0 to 9 mol %. A complex effect of the PEG-coverage was found with a maximum leakage in the range of the transition of the polymer from the mushroom to the brush conformation. The lowest permeabilities for the polymer-grafted vesicles with only a small temperature dependence were measured for the VETs containing 1 mol. % DPPE-PEG, which makes them most appropriate as carriers for drug delivery.

## 417.D3 MOTION OF A MASSIVE PARTICLE ATTACHED TO A LIPID VESICLE

K. Velikov<sup>1</sup>, K. Danov<sup>1</sup>, M. Angelova<sup>2</sup>, C. Dietrich, B. Pouligny<sup>3</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, University of Sofia,  
Faculty of Chemistry, J. Bouchier Ave. 1, 1126 Sofia, Bulgaria.

<sup>2</sup>Institute of Biophysics, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl.21, 1113 Sofia, Bulgaria

<sup>3</sup>Centre de Recherche Paul-Pascal / CNRS, Ave. A. Schweitzer, 33600 Pessac, France

We studied the motion of micro sized spheres (glass or latex particles of diameter 2 to 20  $\mu$ m) attached to lipid membranes of giant phospholipid (Stearoyl-Oleoyl-Phosphatidylcholine) vesicles. A single particle is manipulated by means of an optical trap (1) and brought in contact with a vesicle. The particle adheres to the membrane and locks across the vesicle contour. Detachment or variation of the bead position is not possible perpendicular to the lipid membrane, however the particle can freely be manipulated along the surface of the fluid lipid membrane. The situation is similar to a sphere trapped across the interface of two liquids. In our case the additional lipid layer has to be taken into account.

By applying image processing we recorded the particle tracks when it moves from the top down to the bottom of the vesicle driven by gravity. Due to their high density the observed trajectories of glass particles are essentially sedimentation paths perturbed by Brownian motion. In the case of small latex sphere the Brownian motion dominates the trajectory. We analyzed this problem theoretically and set out a procedure to separate the two contributions and to determine the friction force acting on the particles. Depending on the position of the sphere with respect to the membrane interface, friction values are found to be in the range of 1.1 to 3.5 times to that of particles in bulk water. Applying recent theories for particle motion across viscous interfaces (3) we can separate the contribution to the friction force which is due to the hydrodynamic flow of the solvent (water) and the part which is due to the viscosity of the lipid layer. We obtain values for the membrane shear viscosity on the order of a few poises in agreement with values known from molecular diffusion (4).

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## 418.D3 SPONTANEOUS VESICLES FORMED IN AQUEOUS MIXTURES OF TWO CATIONIC AMPHIPHILES

Maria Isabel Viseu<sup>1</sup>, Silvia M.B. Costa<sup>1</sup>, and Katarina Edwards<sup>2</sup>

<sup>1</sup>Centro de Quimica Estrutural, Instituto Superior Técnico, Lisboa, Portugal

<sup>2</sup>Fysikalisk-Kemiska Institutionen, Uppsala University, Uppsala, Sweden

Spontaneous vesicles have been reported in aqueous mixtures of ionic amphiphiles of opposite charge, either with both single-tailed amphiphiles<sup>1</sup> or with a double-tailed and a single-tailed amphiphile<sup>2</sup>. The thermodynamic stability of these "cationic-anionic" (or "catanionic") vesicles was explained by considering the energy of elastic curvature: the vesicular bilayer will be the more stable phase in solution (as compared to the micellar or lamellar phases) only for special (and different) compositions of the inner and outer layers, which give equal (in magnitude) but opposite spontaneous curvatures<sup>3</sup>.

And what about "cationic-cationic" or "anionic-anionic" vesicles? Can they be spontaneously formed, as well?

The present work reports the formation of spontaneous vesicles in aqueous mixtures of two cationic amphiphiles: the double-chained DDDAB<sup>4</sup> and the single-chained DTAC<sup>4</sup>. The conditions for the formation of an asymmetric bilayer (*i.e.*, with different compositions of the two component layers) are accomplished herein by the different structures of the two cationic amphiphiles, which have quite different "critical packing parameters", *CPP*: in this case, the *CPP*s are  $\sim 2/3$  and  $\sim 1/3$ , for DDDAB and DTAC, respectively.

The first sign of the presence of the vesicles in the system DDDAB-DTAC-water was the readily dissolution in water of the double-chained DDDAB in the presence of DTAC, and the turbidity of the final solutions. The vesicles were then studied by quasi-elastic light-scattering, at several relative molar fractions of the two amphiphiles and in a range of water dilutions: in most cases, the vesicles have mean diameters of ~ 150-200 nm, with a high polydispersity of sizes. The size and morphology of the vesicles in a few samples were analysed by cryo-TEM: the structures observed are mostly spherical, unilamellar vesicles, with a well-defined contour; a few of these are bi- or tri-lamellar., a few ones present open membranes. The cryo-TEM micrographs also confirm the large size polydispersity, with a broad distribution of diameters from ~50 up to ~ 500 nm. The detailed structure of the vesicle walls will be tentatively discussed in this paper.

Even though the open membranes observed in a few samples may indicate an intermediate stage, during, e.g., a vesicle-lamellar phase transition, the composition range of thermodynamic stability of these "cationic-cationic" vesicles seems to be quite large, when compared with their "catanionic" counterparts; another advantage is the easier preparation of these solutions, which does not involve cumbersome precipitation of "catanionic" salts.

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2. E. Marques, A. Khan, M.G. Miguel, and B. Lindman *Self-Assembly in Mixtures of a Cationic and an Anionic Surfactant: The Sodium Dodecyl Sulfate-Didodecyltrimethylammonium Bromide-Water System*, J. Phys. Chem., 97 (1993) 4729-4736.
3. S.A. Safran, P. Pincus, and D. Andelman. *Theory of Spontaneous Vesicle Formation in Surfactant Mixtures*, Science 248 (1990) 354-356
4. DDDAB: *Didodecyltrimethylammonium Bromide*; DTAC: *Dodecyltrimethylammonium Chloride*

## 419.D4

### PHASE BEHAVIOR AROUND TRICRITICAL POINT IN A CATIONIC SURFACTANT SYSTEM

Reiko Aoki and Hironobu Kunieda

*Division of Artificial Environments Systems, Graduate School of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240, Japan*

Three-phase behavior of microemulsion was investigated in a NaBr aqueous solution/hexadecyltrimethylammonium bromide (CTAB)/butanol/decane system at constant temperature, 25°C. Microemulsion coexists with excess water and oil phases when CTAB is changed from water-soluble to oil-soluble with increasing salinity or butanol content. The degree of freedom for the three-phase body is 2 in the present five component system at constant temperature and pressure. Since butanol acts as a cosolvent at low salinity,<sup>1</sup> a decane/butanol weight ratio and salinity are chosen as independent variables. The three-phase body exists between two critical end points of microemulsion-water and microemulsion-oil phases. With decreasing the two variables, two critical end points approach each other and eventually the three-phase body shrinks to a tricritical point at which three coexisting phases simultaneously identical. Beyond the tricritical point (at lower salinity and decane/butanol ratio), the phase transition from aqueous micelles to reverse micelles occurs without passing through the three-phase region. We will discuss the detail phase behavior around the tricritical point in the present system. The effect of temperature on the tricritical phenomenon will be also reported.

1. Kunieda H. and Aoki R., *Langmuir*, 12, 5796 (1996)

## 420.D4

LUMINESCENCE STUDY OF LECITHIN -  
ALCOHOL BASED MICROEMULSIONSS. Avramiotis<sup>1,2</sup>, V. Bekiari<sup>2</sup>, P. Lianos<sup>2</sup> and A. Xenakis<sup>1</sup><sup>1</sup>National Hellenic Research Foundation, Inst. Biological Research & Biotechnology<sup>2</sup>Engineering Science Dept., University of Patras, 26500 Patras, Greece

Water-in-oil microemulsions are fine dispersions of water in nonpolar organic solvents stabilized by surfactants molecules. These systems, also called reverse micelles, are optically isotropic, low viscous and thermodynamically stable solutions. The dispersed water pools can solubilize various biomolecules such as enzymes, which may retain their catalytic ability [1-2]. The presence of enzymes in the microemulsions, results in structural changes of both the biomolecule and the reverse micelles. Most of the studies involving enzyme catalysis in microemulsions have been performed by using AOT, a well characterized synthetic surfactant which forms spherical reverse micelles, and has been considered as a model system for micellar enzymology. Nevertheless, these molecules are generally toxic and cannot be used in potential applications of enzyme containing microemulsions in the pharmaceutical, cosmetics or food technology domains. An attractive alternative could be to use as surfactants natural emulsifiers such as lecithin [3]. For the formation of reverse micelles with lecithin, a forth component, such as an alcohol, has to be added to the system to make the polar aqueous phase less hydrophilic [4].

In the present work water-in-oil microemulsions have been made with lecithin in the presence of various alcohols. The structure of the microemulsions has been studied by steady-state and time-resolved analysis of the luminescence quenching of  $\text{Ru}(\text{bpy})_3^{2+}$  by  $\text{Fe}(\text{CN})_6^{3-}$ . We found that well-defined microemulsions can be made only in the presence of short-chain alcohols such as propanol and butanol. There exists a threshold for water content in order to obtain w/o microemulsions. Thus in the case of propanol, water/surfactant ratio  $w_0$  should be above 20. By varying water content from in the range  $20 < w_0 < 40$ , the microemulsion droplets suffer dramatic structural changes and the system passes trough a percolation threshold.

1. Luisi P.L., Magid L. *CRC Crit. Rev. Biochem.* 1986, 20, 409.
2. Stamatis H., Xenakis A., Provelegiou M., Kolisis, F.N. *Biotechnol. Bioeng.*, 1993, 42, 103.
3. Avramiotis S., Stamatis S., Kolisis, F.N., Lianos P., Xenakis A. (1996) *Langmuir*, in press.
4. Shinoda K., Shibata Y., Lindman B. *Langmuir*, 1993, 9, 1254.

## 421.D4

MICROEMULSIONS AS MEDIA FOR PALLADIUM CATALYSED  
ORGANIC REACTIONS

Cheprakov A.V., Lomakina M.A., Beletskaya I.P.

Department of Chemistry, Moscow State University, Russia

The application of microemulsions as media for transition metal catalysed reactions is described. Winsor I, II, and III type systems based on both anionic and cationic surfactants, as well as Shinoda's swollen micelles of non-ionic surfactants serve as convenient media for carrying out palladium catalysed reactions, such as hydroxycarbonylation, cross-coupling, Wacker oxidation, reductive dehalogenations, arylation of olefins etc. The role of colloidal palladium as a pool of catalytically active species in microemulsion media is discussed.

In contrast to reactions in simple micellar solutions (the so-called micellar catalysis) microemulsions allow to perform reactions on preparative scale comparable to the processes in conventional homogeneous media.

Catalytic processes under consideration are very sensitive to the nature of main surfactant of microemulsion, and depending on the type of catalytic process, different types of surfactants showed the highest performance.

## 422.D4

## SURFACTANT FILMS IN MICROEMULSIONS

Julian Eastoe<sup>1</sup>, Karen Hetherington<sup>1</sup>, David C. Steytler<sup>2</sup>, Richard K. Heenan<sup>3</sup>

<sup>1</sup>*School of Chemistry, University of Bristol, Bristol BS8 1TS UK*

<sup>2</sup>*School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ UK*

<sup>3</sup>*ISIS Facility, Rutherford Appleton Laboratory, Chilton, OXON OX11 0QX UK*

The nature of negatively curved films of di-chained surfactants in water-in-oil microemulsions has been studied by Small-angle Neutron Scattering (SANS). Zwitterionic and ionic amphiphiles with different tail structures were investigated: synthetic C<sub>18:1</sub> phosphatidyl-cholines (PC's) containing C=C bonds, n-alkyl-n-dodecyldimethylammonium bromides (Cn-C12's) and Aerosol-OT. The oil was cyclohexane, but n-heptane for AOT. Various possibilities for solvent penetration into the surfactant film were investigated by model fitting contrast variation SANS data. The most consistent and realistic fit parameters were obtained using a sharp interface model. Although there was no evidence for any hydration layers, the degree of oil penetration was found to increase when the surfactant chains are made more disordered. With C12-C12 and AOT there was no evidence for oil mixing, whereas for PC and C18-C12 layers the results inferred a cyclohexane volume fraction  $\Phi_{C6D12}$  of between 0.05 and 0.20 depending on the surfactant.

## 423.D4 W/O MICROEMULSIONS FROM BINARY IONIC-NONIONIC SURFACTANTS

Hans-Friedrich Eicke and Wolfgang Meier

*Institute of Physical Chemistry, Departement Chemie, Univ. of Basel, CH-4056 Basel, Switzerland*

The addition of a second surfactant to an otherwise thermodynamically stable microemulsion causes interfacial and bulk effects: the combination of AOT and C<sub>12</sub>E<sub>5</sub> supports the formation of planar interfaces (considering the molecular geometries of the surfactants) which induces a sphere to oblate ellipsoid (~disk) transition ensuing a lamellar liquid crystalline phase. Heats of adsorption of C<sub>12</sub>E<sub>5</sub> (adsorbed onto a H<sub>2</sub>O/AOT/i-C<sub>8</sub>H<sub>18</sub> interface) corroborate the existence of two different interfacial states. The phase transition was inferred from combining conductometric and electro-optic Kerr effect studies.

## 424.D4

STRUCTURAL POLYMORPHISM IN QUATERNARY  
NONIONIC MICROEMULSIONS

Shmaryahu Ezrahi, Ellen Wachtel, Abraham Aserin and Nissim Carti

*Faculty of Chemistry, Weizmann Institute of Science, 76100 Rehovot, Israel*

*Casali Institute of Applied Chemistry, School of Applied Science, The Hebrew,*

*University of Jerusalem, 91904 Jerusalem, Israel*

The physico-chemical and structural properties of a quaternary mixture containing the nonionic surfactant C<sub>12</sub>E<sub>8</sub>, water and pentanol/dodecane, at weight ratio of 1:1, was studied.

The work reports results from SAXS, SANS, Cryo-TEM, self-diffusion NMR spectroscopy and other techniques that have been used along the water dilution line with equal weights of surfactant and oil/alcohol. The data provides evidence of the existence, at intermediate water contents, of the so-called "local lamellar" structures, which is an ill-defined bicontinuous mesophase, but lacks the long range order of its liquid crystal analog. Electrical conductivity measurements and expanded X-ray analysis with the use of geometrical mensuration of the O/W micelles and of the hexagonal and lamellar mesophases as an aid in characterizing the microstructures in the isotropic region are presented.



## 425.D4 A NOVEL CALCULATION OF KERR CONSTANTS IN MICROEMULSIONS

J.C. Fernandez, M. Bisceglia and E. Acosta

*Laboratorio de Electrooptica, Facultad de Ingenieria, Universidad de Buenos Aires,  
Buenos Aires, Argentina.*

Microemulsions are transparent dispersions of oil and water, stabilized by adding a surfactant. At low water content, experiments suggest that water in oil (W/O) microemulsions are composed of spherical water droplets dispersed in the continuous oil phase. Each droplet is coated by a film of amphiphilic surfactant molecules, which may be modelled by a hydrophilic polar head in contact with the water surface and a hydrophobic tail in contact with the oil surface. Current literature assigns to this characteristic of the surfactant molecule the property of lowering the interfacial tension between water and oil and hence render possible the formation of the nanodroplets observed in microemulsions.

When an electric field is applied during experiments of Kerr effect, the droplets are polarized and in some cases they lose their spherical shape. Current models for non-spherical droplets assume a prolate spheroidal shape, which is the most simple deformation that can be thought of. These experiments are modelled by the interaction of light with a collection of prolate spheroids, coated with an anisotropic surfactant film.

The polarizability of a homogeneous dielectric ellipsoid immersed in an uniform electric field is found in classical electromagnetics texts. Moreover, it is also found in the literature<sup>1</sup> the same calculation for a coated ellipsoid, when both nucleus and coating are homogeneous and isotropic but with different permittivities. More recently, van der Linden et al.<sup>2</sup> have calculated the polarizability for a homogeneous and isotropic spheroid coated with a thin film with anisotropic, but homogeneous, permittivity. Their model is restricted to thin coatings.

So far to our knowledge no general analysis has been published on the polarizability of coated spheroids for anisotropic coatings of any width, and due to the interest of modelling droplets in microemulsions, we have tried to solve this general problem from first principles.

Laplace equation in spheroidal coordinates is solved to find the analytical expression of the polarizability of a coated spheroid in an uniform applied electric field when the coating presents an anisotropic permittivity. The results agree in the limiting cases of i) negligible coating width, ii) zero eccentricity and iii) isotropic coating with previously published formulae.

This theoretical model is applied in this paper to calculate the birefringence of a W/O microemulsion in terms of the structural parameters of the droplets.

<sup>1</sup> C.F. Bohren & D.R. Huffman, "Absorption and Scattering of Light by Small Particles". Wiley, New York (1983).

<sup>2</sup> E.v.d. Linden, S. Geiger & D. Bedeaux, *Physica A* 156, 130 (1989).

## 426.D4 SOLUBILISATION OF TRIOLEIN IN AN OIL-IN-WATER HYDROCARBON-BASED MICROEMULSION

P.R. Garrett<sup>1</sup>, D. Giles<sup>1</sup>, E. Staples<sup>1</sup>, C.A. Miller<sup>2</sup>

<sup>1</sup>Unilever Research, Port Sunlight Laboratory, Wirral, Merseyside, UK

<sup>2</sup>Rice University, Houston, Texas, USA

An oil/water microemulsion can be prepared from hexadecane and  $C_{12}E_4$ <sup>1</sup>. The solubilisation phase boundaries and cloud points of this microemulsion are separated by about 4-5°C depending upon concentration. Addition of progressively increasing amounts of triolein to the microemulsion moves the solubilisation phase boundary to higher temperatures but has a relatively small effect upon the cloud point. Solubilisation capacity of the microemulsion for triolein therefore increases with increasing temperature up to the cloud point.

Single droplet (of triolein) contact experiments reveal a solubilisation rate which is consistent with activated adsorption at the triolein microemulsion interface. Solubilisation is markedly dependent upon both concentration and temperature. The rate of decrease of droplet sizes is approximately proportional to concentration of the microemulsion and increases markedly as the cloud point is approached. However at

temperatures near to the cloud point of the microemulsion solubilisation is preceded by partitioning of hexadecane into the triolein. Depending upon temperature and concentration this process can be slow relative to solubilisation. In part slow kinetics here are associated with precipitation of cloud phase in the region of the triolein/microemulsion interface. This occurs because loss of hexadecane to the triolein produces a decrease in the cloud point.

1. S.Friberg, I.Lapczynska; *Progr. Colloid & Polymer Sci.*, 56, 16, (1975)

## 427.D4

### PHOSPHOCHOLINES AT OIL-WATER INTERFACES

**Karen Hetherington<sup>1</sup>, Julian Eastoe<sup>1</sup>, Georg Ilgenfritz<sup>2</sup>**

<sup>1</sup>*School of Chemistry, University of Bristol, BS7 ITS, UK.*

<sup>2</sup>*Institut für Physikalische Chemie der Universität zu Köln, D-50939 Köln, Germany.*

We have used Small-Angle Neutron Scattering (SANS) to study phosphocholine (PC) cyclohexane/water Winsor II microemulsions. Two synthetic PCs were used with di-C18 cis or trans surfactant chains, and also naturally occurring Epikuron 200 which contains a mixture of alkyl chains. In each case a core-shell-droplet contrast series of I(Q) data was analysed together in order to reveal the droplet and interfacial structure.

The parameters obtained from these SANS analyses could be used to access film rigidities via:

i) polydispersity and  $\gamma_{o/w}$  measurements  $\rightarrow 2K + K_{bar}$  [1]

ii) transient electrical birefringence measurements  $\rightarrow K$  [2]

Results obtained from these methods will be discussed.

1. a) Gradzielski, M.; Langevin, D.; Farago, B.; *Phys. Rev. E* 1996, 53, 3900.

b) Meunier, J; Lee, L.T.; *Latigmuir* 1991, 7, 1855.

2. Van Der Linden, E.; Bedeaux, D.; Hilfiker, R.; Eicke, H.-F.; *Ber. Bunsenges. Phys. Chem.* 1991, 8, 876.

## 428.D4

### CALORIMETRIC STUDIES ON THE STRUCTURE OF MICROEMULSION WITH NONIONIC SURFACTANT

**Teng Hongni, Teng Dawei, Chen Zongqi**

*Qingdao Institute of Chemical Technology, Qingdao, R. R. China*

Enthalpic studies on the state of water in hexadecane/hexanol/AEO<sub>9</sub>/water system have been conducted. The results indicate that water exists in three states of bound water, trap water and free water. The enthalpic effect of nonionic microemulsion is far below that of ionic microemulsion. On condition that water/oil ratio is in the abnormal rheology region, the negative thixotropy of the system is directly proportional to the enthalpy.

## 429.D4

### UNSTABLE MICROEMULSION STATE OF BINARY LIQUID SYSTEM TRYETHYLAMINE - WATER.

**P.K. Khabibullaev, Saidov A.A., Abdullaev K.A., Tursunov Sh.O.**

*Heat Physics Departuent of the AS of Uzbekistan, 700135, Katartal str., 28, Tashkent.*

In work the influence of external field of disturbance on formation of unstable microemulsion state in liquid binary system tryethylamine-water with bottom critical point of separation was considered. Researchs were conducted by method of adiabatic calorimeter [1]. Decay and mixing of microemulsion states of liquid system of two component solutions was displayed in behaviour of temperature dependence of heat capacity in kind of heat capacity peak and fracture (Fig. 1). The border of instability of forming microheterophase states in dependence on frequency of mixing is discovered (Fig.2). The area of long period

relaxation of microemulsion states is defined between the borders of lability-metastability and metastability-stability states transitions.

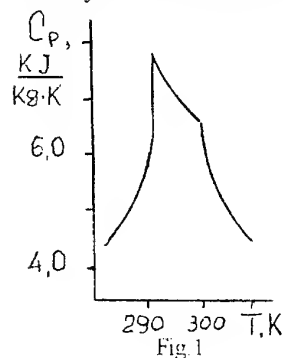


Fig 1

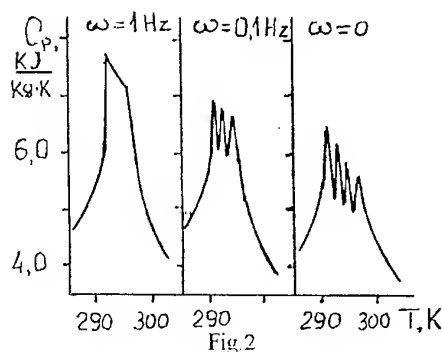


Fig 2

It is determined that with the help of measured outer influence the qualitative and qualitative characteristics of irregular structure forming of microemulsion systems state may be changed.

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### 430.D4 INFLUENCE OF DIFFERENT CHEMICAL TYPE SURFACTANTS ON THE BOUNDARIES OF THE THREE-PHASE SYSTEMS STABILITY

P.M. Kruglyakov, V.D. Mal'kov, T.N. Khaskova

State Academy of Architecture and Building, Penza, Russia

Three-phase systems: water-oil-surfactant phase (micellar phase) can be used for very different purposes. In particular these authors offered the method of stable delute emulsions breaking, which consists in contacting of emulsions with the micellar phase. By mixing of emulsion with the micellar phase the main part of surfactants is absorbed in the micellar phase and the excess water and oil are given off as delute surfactant solutions in water and in oil.

As a result of the accumulation of surfactants in the micellar phase during breaking of emulsions the micellar phase becomes unstable. So the main problem in using of this method is ensuring of the conditions, at which the three-phase system keeps stable and the micellar phase is not mixed with water and oil.

Aiming at this, we investigated the influence of hydrophilic-lipophilic balance and chemical type of surfactants on the boundaries of the existence of the micellar phases.

The micellar phases were obtained from ionic (sodium dodecyl sulfate, cetyl pyridiniumchloride with additive of alcohols and electrolytes) and nonionic (oxyethylenedoctylphenols and acids and sorbitan oleate) surfactants. Affinity of the surfactants to water and oil was characterised through the hydrophilic-lipophilic ratio (HLR), which is expressed as a ratio of interaction energy of the polar and apolar parts of surfactant with water and oil and through the partition coefficient ( $K_{wo}$ ) for surfactant between oil and water expressed as a ratio of molar concentrations.

At the same values of HLR and  $K_{wo}$  the surfactants of different chemical types were shown to influence differently on micellar phase stability. All the alcohols with  $K_{wo}$  less than 6 promote separating of water from middle phase, but micellar surfactants with the same  $K_{wo}$  yield separating of oil.

It means that the boundaries of existence of the three-phase system depend not on the HLR surfactants only but on the chemical type of surfactants too.

### 431.D4 LIGHT SCATTERING STUDY OF ISOCTANE/AOT MICROEMULSIONS: CLUSTER FORMATION IN NON-AQUEOUS AND IN WATER/POE SYSTEMS

César A.T. Laia<sup>1</sup>, Wyn Brown<sup>2</sup>, Mats Almgren<sup>2</sup> and Sílvia M.B. Costa<sup>1</sup>

<sup>1</sup>Centro de Química Estrutural, Complexo 1, Instituto Superior Técnico, 1096 Lisboa Codex, Portugal;

<sup>2</sup>Institute of Physical Chemistry, University of Uppsala, Box 532, 751 21 Uppsala, Siveden.

Previous work in oil-continuous Isooctane/AOT microemulsions with non-aqueous polar solvents showed that in these systems attractive forces between the droplets are greater than in water-in-oil microemulsions [1]. This leads to the formation of clusters of reversed micelles at low dispersed phase volume fractions and to a decrease of the percolating temperature threshold. The clustering is a general

property of microemulsions and is favoured when polar solutes such as Urea and Formamide are added to water-in-oil microemulsions[2].

Another type of clusters exist when water soluble polymers, with sizes larger than the water pool, are added into these systems. In this case there is formation of higher order aggregates with the polymer making the backbone; however the increase of the surfactant monolayer elastic bending, rises the percolation temperature threshold caused by adsorption of the polymer in the interface as observed in poly(oxyethylene) (POE) systems [3].

Using Light Scattering techniques, the two clustering processes were studied in oil-continuous Isooctane/AOT microemulsions. In non-aqueous microemulsions entrapping Glycerol and Formamide there was evidence of the first type clusters formation. These systems have a bimodal diffusion coefficient distribution: one related to the individual aggregates and the other one to the collective diffusion of the aggregates. The slow diffusion is dependent on both temperature and dispersed phase volume fraction.

Another study of water-in-oil microemulsions with POE was made with different polymer molecular weights (3000, 35000 and 300000 D) and with different  $w_o$  (where  $w_o = [Water]/[AOT]$ ). The results show that when the polymer size cannot fit the water pool there is cluster formation with the polymer making the backbone. In this case the slow diffusion coefficient has a different behaviour because it is relatively insensitive to the dispersed phase volume fraction. When the polymer fits the water pool, the microstructure is very similar to the one observed in Isooctane/AOT/Water systems, and a decrease of the aggregation number is observed with a increase of the aggregate polydispersity. An interesting result was obtained for POE with 35000 D of molecular weight, showing at  $w_o = 35$  a very narrow transition between these two behaviours.

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2. Garcia-Rio, L.; Leis, J.R.; Mejuto, J.C.; and Peña, M.E., *Langmuir* 1994,10, 1676-1683;
3. Meier, W.; *Langmuir* 1996,12, 1188-1192.

## 432.D4

### INTERACTION OF MEDIALY HYDROPHOBIC WEAK ACID-BASE PAIRS WITH MICRO-EMULSIONS

Lopes, A., Melo, E.

*Inst.Tecnol Quimica e Biológica - Ap. 127, P-2780 Oeiras, Portugal*

Most part of biological processes and abiotic transformations in natural media involve reactions at the surfaces of micro-aggregates of amphiphilic substances - phospholipid membranes, skin, plant cuticle, natural or man made surfactants, humic and fulvic substances, etc. Microemulsions with two distinct bulk phases compartmentalised with one complex soft interface of amphiphilic substances appears as the most simple systems where we can mimic those natural occurring aggregates.

In spite of being hydrophobic a large number of organic xenobiotics - usual drugs and pollutant materials - undergo acid-base equilibria under physiological and environmental pH conditions. So, a simple hydrophobicity criteria is not applicable to predict the interaction of those xenobiotics with biota or lipidic abiotic material because both their charged,  $DH^+$ , and unchanged, D, forms may interact with the different "reservoirs" in the micro-aggregates (Lopes, A. *et al*, *Environ.Sci. Technol.*, 26 (1992), 2448).

In this work, we study the effects of pH and ionic strength on the distribution of both neutral and charged forms of a set of pesticides with  $pK_a$  near the environmental and physiological conditions in the different "reservoirs" of micro-emulsions. In order to cover the entire range of aggregates surface charge density we have used w/o micro-emulsions systems with zwitterionic phospholipid -lecitin-, neutral- $C_{12}E_4$  and  $C_{12}E_{10}$  - and charged -AOT-surfactants in various organic solvents and  $w_o$  values.

The methods used for the localisation of D and  $DH^+$  are based upon the photophysical properties of the drugs -fluorescence lifetime, fluorescence quantum yield and fluorescence anisotropy (Lopes, A., *et al.*, *Environ. Sci. Technol.*, 29 (1995), 562).

Moreover, the model takes into account the partition of the drugs between water, the interface and the hydrophobic regions of the system, and the effects of the various properties affecting them: pH, ionic strength, and local dielectric constant. Surface potential is discussed accordingly to *Poisson-Boltzmann*

equations based upon the dimension of the "pools" followed by static and dynamic LS, and binding of counter-ions followed by  $^{23}\text{Na}$  NMR (Kenéz, P., *et al.*, *J. Phys. Chem.* 96 (1992) 9524).

### 433.D4 MICROEMULSIFICATION OF VARIOUS NATURAL OR SYNTHETIC RESINS IN WATER SOLUTIONS OF SURFACTANTS OF DIFFERENT PH - VALUES

N. Lysogorskaya

*St. Petersburg State Technological University of Plant Polymers, Russia*

Colloid solubilization phenomenon has been discovered and studied for various solid-soft substances (resins in wood and cellulose, white resin, mastic, polyethylene, polystyrene, as well as epoxy resin phenol-formaldehyde resin, etc.) in solutions of surfactants (sodium tetrapropylene-benzenesulfonate and dibutyl-naphthalenesulfonate, trimethyloctadecylammonium chloride, polyethylene glycole and alkylphenole ethers).

Electron microscopy and dynamic light scattering in micellar solutions of surfactants, and adsorption compounds consist of the listed substances and surfactants in solutions, and also those dispersed in water without surfactants, together with investigations on solubility temperature-time curves for a wide range of surfactant concentrations and solubility dependences on starting weight dispersities, allow to conclude that the process starts with sample dispersing, while at its end high-micellar solutions occur where microemulsions are formed, their size being comparable with size of surfactant micelles themselves. Surfactant nature and micelles formation ability are shown to be the most important factors of resin solubilization, the more micellar surface, the higher solubilization rates.

It has been shown for the example of wood resin, that abrupt increase of solubility starts when surfactant concentration exceeds a critical concentration of micelle formation about tenfold, especially if the media are not neutral (pH 2 and pH 10 or higher). Investigations on colloid-chemical solubility characteristics (resin/liquid interfacial tension, surface energies of dissolved particles, process activation energy) show that this is caused by appearance of lyophilic properties of the systems and formation of microemulsions showing thermodynamic stability and having interfacial tensions not over 0.1 mJ/m<sup>2</sup>.

### 434.D4 MORPHOLOGICAL MODEL FOR COMPLEX FLUIDS

K. R. Mecke

*Fachbereich Physik, Bergische Universität Wuppertal, D-42097 Wuppertal, Germany*

The homogeneous spatial domains of phases on a mesoscopic scale are a characteristic feature of complex fluids and porous media. For instance, microemulsions exhibit a bicontinuous structure of homogeneous oil and water phases stabilized by amphiphilic surfactants assembled at the oil-water interface. The thermodynamics and bulk properties of such composite materials depend often on the morphology of its constituents, i.e. on the spatial structure of the homogeneous domains. Therefore, a statistical theory should include geometrical as well as topological descriptors to characterize the size, shape and connectivity of the aggregating mesophases in such media.

We propose a new model for studying porous media and complex fluids using morphological measures to describe the homogeneous spatial domains of the constituents. Under rather natural assumptions a general expression for the Hamiltonian can be given by extending Widom and Rowlinson's model for penetrable spheres. The Hamiltonian includes energy contributions related to the volume, surface area, mean curvature, and Euler characteristic of the configuration generated by overlapping sets of arbitrary shapes. Phase diagrams and structure functions of the model are calculated and discussed. In particular, we find that the Euler characteristic in the Hamiltonian stabilizes a highly connected bicontinuous structure resembling the middle-phase in oil-water microemulsions. We present first results of Monte-Carlo simulations and discuss some applications to colloidal systems and porous media.

**435.D4 POLYMERIZABLE SURFACTANTS IN W/O MICROEMULSIONS****N.Moumen<sup>1</sup>, M.P. Pileni<sup>2,3</sup>, F. Pavel<sup>1</sup> and R.A. Mackay<sup>1</sup>**<sup>1</sup>*Center for Advanced Materials Processing, Clarkson University, Potsdam, NY 13699- 5665, USA*<sup>2</sup>*Laboratoire SRSI, URA 1662, Université Pierre & Marie Curie, BP 52, 4 place Jussieu, 75231 cedex 05, France*<sup>3</sup>*C.E.A.Saclay, DRECAM. S. C.M., 91191 Gif sur Yvette, Cedex, France*

Polymerization in microemulsions has been largely studied in the last 15 years in the case of oil in water systems, but in case of water in oil microemulsions, polymerization has been studied only by a limited number of authors. This work is an extension of a study on the polymerization of didecyldimethylammonium methacrylate in reverse micelles recently reported by Pileni, et. al.

Didecyldimethylammonium methacrylate forms W/O microemulsions, with water and methacrylate in dispersed phase and an oil such as toluene being the continuous phase. These W/O microemulsions have been irradiated in the presence of various initiators, and the resulting polymerized latex particles characterized by dynamic light scattering (DLS) and transmission electron microscopy (TEM). The particle size distribution is polydisperse, and in the range of 3-10 nm in suspension. The average diameter decreases with the TEM, indicating that the dispersed latexes are swollen with water. Some studies have also been carried out on the polymerization of sodium acrylate taken up by the swollen particles, resulting in a larger composite aggregate. Initial studies have been carried out using a polymerizable oil in a W/O microemulsion with the objective of producing a clear solid. As expected, phase separation tends to occur during polymerization. The results of these studies will be presented and discussed.

**436.D4 AN ESR STUDY OF THE EFFECT OF NON-IONIC COSURFACTANTS ON AOT REVERSED MICELLES****Luis M.M. Nazário<sup>1</sup>, José J. G. Moura<sup>1</sup>, T. Alan Hatton<sup>2</sup>, João P.S.G. Crespo<sup>1</sup>**<sup>1</sup>*Dept. Química, Fac. Ciências e Tecnologia, Universidade Nova de Lisboa, 2825 Monte de Caparica, Portugal*<sup>2</sup>*Massachusetts Institute of Technology, Chemical Eng. Dept., Bldg. 66-309, Cambridge, MA 02139, USA*

Reversed micelles are complex systems in which nanometer-sized water droplets are solubilized in an apolar solvent. Electron Spin Resonance is particularly suitable to study these systems. The fact that spin probes with different chemical structures (and polarities) are available is extremely useful because information on the different environments can be obtained by selecting an appropriate, probe.

This communication will discuss the effect on the local structuring and polarity due to the change in interfacial composition of AOT reversed micelles when a non ionic cosurfactant is added to the system. Two types of cosurfactants were used: linear chained alcohols and poly(oxyethylene)alkyl ethers. The spin probes were chosen so as to obtain information on the water pool and the interfacial headgroup and tail regions. Besides the effect of the interfacial composition, the effect of micelle size and ionic strength was also studied.

**437.D4 A FLUORESCENCE STUDY OF THE PHASE BEHAVIOUR OF THE THREE COMPONENT SYSTEM C<sub>12</sub>E<sub>5</sub>/WATER/ALKANE****M.E.C.D. Real Oliveira<sup>1</sup>, M.S.A. Correia<sup>1</sup>, H.D. Burrows<sup>2</sup>, M.da G. Miguel<sup>2</sup>.**<sup>1</sup>*Departamento de Física, Universidade do Minho, Portugal*<sup>2</sup>*Departamento de Química, Universidade de Coimbra, Portugal.*

Interesting phase behaviour is shown by systems containing the nonionic surfactant C<sub>12</sub>E<sub>5</sub> (C<sub>12</sub>H<sub>25</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>5</sub>OH) in the presence of water and an alkane. Over a certain composition range these form microemulsions which are bicontinuous in both oil and water. Phase diagrams and self diffusion coefficients

of the three components have previously been reported for the systems with the alkanes heptane, decane and tetradecane<sup>1</sup>. However, in spite of the potential theoretical and practical importance of such bicontinuous systems, a number of questions on both structure and dynamics remain unanswered. We address some of these using the fluorescent probe pyrene. Absorption and fluorescence spectra have been studied as a function of temperature and composition. Abrupt changes in the  $I_1/I_3$  fluorescence intensity ratio, and in the relative yields of monomer and excimer fluorescence are observed at temperatures corresponding to the phase transitions. These depend markedly on the chain length of the hydrocarbon phase, and show that fluorescence provides a good way of determining the phase boundaries. Differences are observed in fluorescence excitation spectra for monomer and excimer, and in the wavelength of excimer emission over the temperature range corresponding to the phase transition, suggesting that both pyrene excimer and aggregates are being formed. This is supported by absorption spectral data, and implies that both fluidity and polarity change on going through the phase transitions. Further information on the diffusion behaviour is obtained by dynamic measurements. The results will be discussed in terms of possible models for the bicontinuous phase.

1. U. Olsson, K. Shinoda, and B. Lindman, *J. Phys. Chem.* 1986 90, 4083-4088.

#### 438.D4

##### BIOCATALYSIS USING GELATIN MICROEMULSION-BASED ORGANOGELS

Gareth D. Rees\*, Tuah R-J Jenta and Brian H. Robinson

*School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, UK*

Biotransformations involving lipases have been widely studied over the last decade. Their utility in the food industry for fat modification and flavour production is widely recognised and lipases have made a tremendous impact in the field of regioselective and stereoselective preparative organic synthesis. Various methodologies exist in the literature for effecting biotransformations using cell-free enzymes in apolar media, however one of the most intensively studied has been the technique of solubilising enzymes in hydrated reverse micelles or water-in-oil (w/o) microemulsions. A major attraction of this procedure is that the enzyme is dispersed at the molecular level, rather than as an aggregate of clustered enzyme, in a thermodynamically stable liquid medium which is capable of solubilising polar, apolar and interfacially active substrates. Interestingly, w/o microemulsions can form thermoreversible organogels on addition of the water-soluble biopolymer gelatin, and the resulting materials provide a novel bio immobilisation matrix. The microemulsion-based organogel (MBG) matrix is stable on contact with a polar solvents and under most conditions fully retains the surfactant, gelatin, and water components. We have demonstrated its utility as an enzyme immobilisation matrix, and in pelleted form it can be used as a solid phase biocatalyst in the presence of organic solvents or liquid substrates. MBGs offer considerable advantages over w/o microemulsions in that much higher enzyme loadings are achievable than is the case with their liquid phase counterparts, and product isolation and enzyme reuse is facilitated. In the present study we have characterised the catalytic behaviour of MBG formulations containing immobilised *Chromobacterium viscosum* (CV) lipase where aspects of both activity and stability of the immobilised enzyme system were addressed.

#### 439.D4

##### MICROEMULSION SYSTEMS STABILIZED BY DIALKYLDIMETHYLAMMONIUM BROMIDES

Adam Sokolowski, Kazimiera A. Wilk, Bogdan Burczyk

*Institute of Organic and Polymer Technology, Technical University of Wrocław,  
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

Phase behavior of dialkyldimethylammonium bromides (alkyl: R = n-C<sub>8</sub>H<sub>17</sub>; n-C<sub>10</sub>H<sub>21</sub>, and n-C<sub>12</sub>H<sub>25</sub>) in alkane/water systems within the temperature range of 20-50°C has been studied. The microemulsions structure has been characterized by means of interfacial tension, coacervation, and chemical composition of the microemulsions formed.

The effects of the type of both alkane and salt on the monolayer structure and the so-called surfactant or third phase formation have been discussed. The observed Winsor III system is governed by the following rule: the lower is the salt concentration, the longer alkyl chain of the surfactant under study is needed. Winsor - transformations were accompanied by changes of the surface and interfacial tensions. The lowest interfacial tensions (below  $0.01 \text{ mNm}^{-1}$ ) were observed for didodecyldimethylammonium bromide which is responsible for the formation of vesicular solutions or random lamellar  $L_3$  phase. In the case of dioctyldimethyl ammonium bromide the interfacial tensions reach at most  $0.5 \text{ mNm}^{-1}$ .

#### 440.D4

##### AMMONIUM DI(ETHYLHEXYL) PHOSPHATE: A NEW SURFACTANT FOR MICROEMULSIONS

David C. Steytler<sup>1</sup>, D. Lee Sargeant<sup>1</sup>, Gabriel Welsh<sup>1</sup>, Brian H. Robinson<sup>1</sup>, and Richard K. Heenan<sup>2</sup>

<sup>1</sup>School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

<sup>2</sup>ISIS, Rutherford Appleton Laboratory, Chilton, OXON OX11 0QX.

The ammonium salt of the metal-ion extractant di(ethylhexyl)phosphoric acid (HDEHP) has been found to stabilise water-in-oil (w/o) microemulsions over a wide range of  $\omega$  ( $= [\text{H}_2\text{O}]/[\text{NH}_4\text{DEHP}]$ ) and temperature. Such extensive solubilisation has not been observed for Gp I, II or III metal salts of HDEHP. Binary  $w_{\text{max}}$  - T phase diagrams for  $\text{NH}_4\text{DEHP}$  w/o microemulsions in n-alkanes cover a wide range of droplet size ( $\omega_{\text{max}} < 100$ ) and temperature (0 - 90°C).  $\text{NH}_4\text{DEHP}$  therefore has advantages in applications where high levels of water solubilisation are required with good thermal stability.

SANS measurements show that, in the absence of water,  $\text{NH}_4\text{DEHP}$  forms extended rod-shaped reversed micelles in oil media of length,  $L > 300$ . As water is added the micelles become progressively shorter in length until spherical droplets are formed at  $\omega \sim 4$ . With further addition of water the droplets grow in size with the core radius  $R_c$  increasing in proportion to the water content,  $\omega$ .

Unlike the surfactant Aerosol OT, which is readily hydrolysed,  $\text{NH}_4\text{DEHP}$  is chemically stable under basic conditions and may be a better choice of surfactant in applications of w/o microemulsions at elevated pH. Conversely, the high  $\text{pK}_a$  of the parent acid, HDEHP, confers instability under mild acid conditions resulting in separation of the dispersed aqueous phase. However the reversibility of this instability provides a novel route for facile separation of solubilised components in the microemulsion droplets which may prove a valuable asset in microemulsion-facilitated separation processes.

#### 441.D4

##### ABNORMAL DIELECTRIC RESPONSE OF AEROSOL OT W/O MICROEMULSION IN CYCLOHEXANE

Reiji Tanaka

Department of Chemistry, Faculty of Science, Osaka City University,  
Sugimoto, Sumiyoshi-ku, Osaka, Japan 558

A dielectric constant  $\epsilon$  for W/O microemulsions consisting of sodium bis (2-ethylhexyl) sulfosuccinate (AOT), water and cyclohexane was measured at a frequency 1 MHz and at a temperature 298.15 K. A resonance method was applied to measure  $\epsilon$ . A stepwise dilution technique was used to prepare mixtures. With a constant molarity of AOT, the value of  $\epsilon$  increases with an increasing mole ratio  $r$  of water added to AOT. There appears a region where the dielectric constant is kept nearly constant around  $r \sim 10$ . Those abnormal changes in  $\epsilon$  are discussed in terms of apparent dipole moment of reversed micelles and the hydration of polar group of AOT. The effects observed due to addition of salt and  $\text{C}_{10}\text{H}_{21}\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$  as a cosurfactant will be reported. The present results will be compared with those reported previously<sup>1</sup>.

I. R. Tanaka, K. Okazaki, and H. Tsuzuki, Abnormal Dielectric Response of Aerosol OT W/O Microemulsion in Cyclohexane at 298.15 K. *Chem. Letters* 1995, 113 1.



#### 442.D4 SURFACTANT FILM ADSORPTION BEHAVIOUR OF A HYDROPHOBIC SOLUTE IN BICONTINUOUS MICROEMULSION

F. Testard, Th. Zemb

*C.E.A., D.R.E.C.A.M./S.C.M., CE Saclay, bat. 125, laboratoire de Diffusion de Rayonnement X aux Petits Angles, 91191 Gif sur Yvette, France.*

We choose the model system involving a common hydrophobic pesticide "lindane" ( $C_6H_6Cl_6$ ) in a ternary microemulsion made with nonionic surfactants. The solubilisation of lindane in the surfactant film is studied as the adsorption of a gas on a solid. The "gas" phase is the oil, whether the surfactant film is analogous to the surface of a solid.

We observed and quantified by three experimental methods an excess of solubilisation of lindane in the film of the microemulsion compared to the maximum solubility of lindane in the pure oil. This "excess" is understood as an adsorption of the solute on the surfactant film analysed in terms of a molar rate lindane/surfactant in the film (of the order 0.3). A curve similar to a gas adsorption isotherm on a surface has been determined. This curve depends of the "penetrating" character of the oil chosen for the microemulsion and inducing different variations of spontaneous curvature.

By small angle scattering and phase diagram determination we determined the location and the structural modifications of the surfactant film induced by the presence of the solute molecule in the film. We propose a linear relation between the amount of solute adsorbed on the film and the induced spontaneous curvature variation of the surfactant film. This relation describes the solubilisation of lindane before the saturation of the microemulsion and can be understood by geometrical considerations.

For microemulsion saturated with lindane, we observed that the ratio lindane/surfactant in the film depends of the spontaneous curvature of the film.

The thermodynamical and structural method used in this model case can be generalised to study the adsorption of neutral solute in bicontinuous microemulsion, connected cylinder or sponge phases.

#### 443.D5 CRYSTALLINE COLLOIDAL ARRAY NONLINEAR-OPTICAL SWITCHING MATERIALS

Sanford A. Asher, Rasu Kasavamoorthy, and Guisheng Pan

*Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260*

We have developed nonlinear optical switching devices from crystalline colloidal arrays polymerized in hydrogels. In one approach we synthesize monodisperse, highly charged colloidal particles with covalently attached dyes from fluorinated acrylamides. These particles have extraordinarily low refractive indices. These colloids self assemble into a crystalline colloidal array and the polymerizable acrylamide monomers in the medium are polymerized to form a hydrogel. The hydrogel medium is altered by solvent exchange, such that the medium has a refractive index that exactly matches the colloidal particles. Thus, at low light intensities the crystalline colloidal array is invisible to light and does not diffract. At high incident intensities the particles absorb sufficient light to heat up within nsecs. This results in a refractive index mismatch between the particles and the medium. The array "pops up" to diffract light meeting the Bragg condition. This material acts as a nsec optical switch. We will discuss the switching behavior and utility of these materials in optical devices.

In another embodiment we have created highly charged, monodisperse silica spheres containing monodisperse CdS quantum dots. The electronic nonlinearity of these quantum dots is used to drive a crystalline colloidal switching array.

## 444.D5

A MOTIF FOR NOVEL SENSORS: INTELLIGENT  
POLYMERIZED CRYSTALLINE COLLOIDAL ARRAYS

John H. Holtz and Sanford A. Asher,

*Department of Chemistry, University of Pittsburgh, Pittsburgh PA 15260 USA*

We have created a novel chemical sensor material utilizing a crystalline colloidal array (CCA) of polystyrene colloids polymerized in an intelligent hydrogel. The CCA self assembles from a suspension of highly charged, monodisperse polystyrene colloids to yield a colloidal suspension with a mesoscopic periodicity. We add water soluble, polymerizable monomers to the CCA suspension and polymerize various types of hydrogels around the array. The lattice spacing of the CCA is on the order of the wavelength of visible light, so the sensor Bragg diffracts light at a wavelength determined by the interparticle spacing of the CCA, which is proportional to the gel volume. In our sensor, the intelligent hydrogel contains a molecular recognition element; in the presence of the recognized substrate, the gel swells (Fig.1). The diffracted wavelength sensitively reports on the gel volume, and hence on the concentration of recognized substrate.

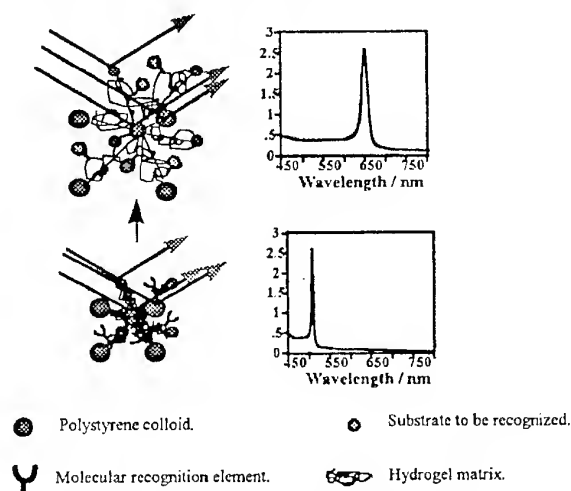


Figure 1. Intelligent polymerized CCA response to a recognized substrate.

We fabricated a sensor, utilizing acryloylamido-benzol18-crown-6 as the chemical recognition element, that selectively detects  $Pb^{2+}$  in a concentration range of 2  $\mu M$  to 10  $\mu M$ . We also fabricated a sensor, utilizing glucose oxidase as a biochemical recognition agent, that detects 100  $\mu M$  to 500  $\mu M$  glucose. The response time for the 125  $\mu m$  thick  $Pb^{2+}$  sensor in 1 mM  $Pb^{2+}$  is within 30 seconds; a 125  $\mu m$  thick glucose sensor responds to 1 mM glucose within 2 minutes. The response time can be decreased by decreasing the thickness of the gel. We have attached these materials to the end of an optical fiber to create a novel optrode sensor.

## 445.D5

THE CONTROL OF ALUMINIUM MODIFIED ZIRCONIUM  
PHOSPHATE GEL POROSITY AND TEXTURE

T.F. Kouznetsova\*, S.I. Yermenko, G.S. Lemeshonok

*Institute of General and Inorganic Chemistry, Byelorussian Academy of Sciences, Minsk, Belarus*

The present report is devoted to sorption structural studies carried out on a number of aluminium modified zirconium phosphate gels prepared from aluminium and zirconium chlorides by the adding either aqueous ammonia or ammonium carbonate.

Carbon tetrachloride and water vapour sorption, BET surface area measurements, X-ray diffraction, derivatography techniques were used to study variations in the texture of aluminium-zirconium phosphates. A series of coprecipitated gels was obtained at constant pH by adding two aqueous solutions containing ammonia (ammonium carbonate) and phosphoric acid to the aqueous solution containing Zr and Al chlorides in various per cent ratios. The gels were dried at 393 and 923 K.

The gels exhibited a wide range of different pore textures extending from micropores to wide mesopores. It has been suggested that the development of the gel porosity appears to have been controlled by the mode of enlargement of the micropore volume being obtained by exchanging interlayer ions of zirconium phosphate with polyoxocations containing aluminium. At appropriate Zr/Al percentage was found the most expanded pore texture with high overall surface areas.

**446.D5****A LIQUID CRYSTAL PHASE IN ORGANIC MEDIUM****M. Morvan<sup>1</sup>, G. Guérin<sup>1</sup>, A. Bauer<sup>1</sup>, M. Dubois<sup>2</sup>, Th. Zemb<sup>2</sup>**<sup>1</sup>*Rhône Poulenc, Centre de Recherches d'Aubervilliers 52, Rue de la Haie Coq,  
93308 Aubervilliers Cédex - France*<sup>2</sup>*CEA, C.E. Saclay, Service de Chimie Moléculaire, 91191 Gif sur Yvette Cédex - France*

In aqueous surfactant mixtures, viscoelastic properties are frequently observed due to cylindrical microstructures as giant micelles or multilamellar crystallites of a dispersions in organic solvents, relevant in various chemical formulations. For instance, they can be used as suspending media for solid particles such as mineral compounds in organic antifoams or active ingredients in agrochemicals formulations

Here instead of the classical reverse micellar isotropic fluid observed with the twin tailed anionic surfactant sodium bis (2-ethylhexyl) sulfosuccinate (AOT) in organic solvents, we report using sodium benzoate the formation of a lyotropic phase. A gel occurs in an hydrocarbon type solvent (solvesso 150®), upon heating around 70 °C and cooling a mixture of AOT and sodium benzoate.

The ternary phase diagram of AOT - sodium benzoate - "solvesso®" was determined. The extension of the gel domain depends on the concentration ratio between AOT and sodium benzoate. Small angle X-ray scattering was employed to investigate the gel structure at a colloidal scale, using a pinhole geometry SAXS camera. Scattering experiments were performed on various samples following dilution paths in the phase diagram. The same scattering pattern was always observed for gels indicating a biphasic dispersion. Indexing of X-ray diffraction data suggests a liquid crystal cubic phase with a periodicity of 5 nm. Determination of the viscoelastic behavior was also consistent with such a cubic phase. The gels are then biphasic systems, the cubic phase being in equilibrium with an excess of solvent. The average size of the heterogeneties was estimated by the asymptotic law derived from ultrasmall angle X-ray scattering measurements.

The peculiar behavior where a stiff cubic phase from the skeleton of a large volume of imbedded oil, is only controlled by the exchange from the usual sodium counter-ion to sodium benzoate which associates counter-ion as well as cosurfactant properties.

**447.D5****THE MECHANISM OF FORMATION OF MESOPOROUS SILICA:  
STRUCTURAL ORGANIZATION OF SILICATE POLYANIONS WITH SURFACTANTS****Svetlana Pevzner and Oren Regev***Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel*

A novel family of mesoporous molecular sieves (M41S) has recently been reported by scientists of Mobil Oil Research and Development. The synthesis is based on gelation of inorganic compound (silica in most cases) around surfactant aggregates (micelles) acting as a templating agent. The mechanism of formation is not yet completely understood. We aim at studying the mechanism and the phase transitions occurring during mesoporous material formation.

A few derivatives of mesoporous materials have been obtained: Lamellar, micellar cubic, bicontinuous cubic and hexagonal liquid crystalline phases. In general, the structure of the aggregates depends, among other factors, on their geometrical properties, i.e., surfactant packing parameter. The effective head group area depends on a few parameters: surfactant concentration, temperature, presence of inorganic or organic additives and others. In the particular case of M41S some additional parameters are considered: the silica concentration and its gelation rate on the aggregate surface, and the surfactant/inorganic molar ratio.

We present here an in-situ phase transition study (using small angle X-ray scattering (SAXS)) during two preparation procedures of bicontinuous cubic (Ia3d) phase. In procedure A we use NaOH as a base, where in procedure B an organic base is applied. In A we found a lamellar-hexagonal-cubic phase transition sequence, and in B a hexagonal-lamellar-cubic transition occurred. The results are discussed in term of geometric parameters.

**448.D5****POLYMER -WATER INTERACTIONS IN HYDROGELS****P. Pissis, A. Kyritsis, A.A. Konsta and D. Daoukaki***National Technical University of Athens, Department of Physics, Athens, Greece*

Hydrogels are cross-linked hydrophilic polymers which imbibe substantial amounts of water, but which swell rather than dissolve in water. The physical structure and the properties of water in hydrogel are primarily determined by the existence of binding sites in the polymer and by geometrical confinement.

We report here on the hydration properties of three different hydrogel systems, studied by means of dielectric techniques, as well as equilibrium and dynamic water sorption isotherm measurements. The systems are (a) poly(hydroxyethyl acrylate) (PHEA), (b) interpenetrating networks of poly(ethyl acrylate) and poly(hydroxyethyl methacrylate) (PHEA/PHEMA IPNS), and (c) polyacrylamide (PAA). The dielectric techniques used include broad band dielectric relaxation spectroscopy (DRS) in wide ranges of frequency ( $10^{-2}$  Hz - 20 GHz) and temperature (173 - 363 K), and thermally stimulated depolarization currents (TSDC) techniques in the temperature range 77 - 300 K.

The results of water sorption measurements are interpreted in terms of mobile and immobile water (free and bound), and clustered water at high relative humidities. The dielectric techniques allow to look at the mobility of water itself and the influence of water on the relaxation and conductivity mechanisms of the polymer matrix. Their results are interpreted in terms of classification of water into different fractions, in irrotationally (tightly) bound, loosely bound and free (bulk) water, when looking at the reorientation of water molecules themselves, and in plasticizing and non-plasticizing water, when looking at the influence of water on the relaxation of the material constituents.

**449.D5****SOL-GEL-TRANSITION IN SOLUTIONS  
OF BASIC ALUMINIUM CHLORIDES****D. Salah, O. Seidel, P. Brand, H.-J. Mögel***Freiberg University of Mining and Technology, Institute of Physical Chemistry, D-09596 Freiberg, Germany*

In addition to their application in deodorant basic aluminium chlorides solutions are of great importance for preparation from aluminium oxide phases. Applying thermal decomposition aluminium chloride gels could be transformed to corundum already at 400°C, whereas the same process with other aluminium compounds is in the rule only over 1000°C to realise. The corundum content applying sol-gel process depends on the method of preparation, on the basicity of the sol and on the gel building condition.

The reported results show that primary particle distribution is responsible for the building of the gel, which are transformed to corundum after calcination. The particle size distribution in the polyoxy cation complex and the agglomerate have been measured by dynamic light scattering. The transformation to gel was realised at 20°C through the evaporation of the suspending agent. The sol-gel-transition has been followed with viscosity and viscoelasticity measurements as well as with the determination of the time correlation function of the light scattering intensities. A competition between chemical condensation reaction and physical agglomeration has been observed. The processes differ by their time constant. The obtained gel depends on, which process dominates.

Each of the differently prepared sols and the obtained gel show anisometric structure, that has been characterised through electron optic as well as polarisation microscopic detection. In addition structural differences of surfaces has been shown by AFM-Tools.

By means of the characterisation of the sol, and the examination of gels after variations of the sol-gel-transition, it has been established which sol structure and sol-gel-transition conditions are responsible for corundum building after calcination. The techniques used are rheometry, dynamic and static light scattering, polarisation microscopy, electron microscopy and AFM.

We gratefully acknowledge financial support from the Fond der Chemischen Industrie.

## 450.D5 EFFECT OF DONNAN OSMOTIC PRESSURE ON THE VOLUME PHASE TRANSITION OF N-ISOPROPYLACRYLAMIDE GELS

Shigeo Sasaki, Hideya Kawasaki and Hiroshi Maeda

*Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka, 812, Japan*

N-isopropylacrylamide gel is well known to exhibit volume phase transition, discontinuous volume change with temperature. The volume phase transition behavior has been believed to be more evoked by introducing the Donnan osmotic pressure into the system, after it has been reported that copolymer gel of NIPA and acrylate (NIPA-AA) at the neutral pH shows larger volume change at higher transition temperature. However, recently it has been reported that copolymer gel of NIPA and charged comonomer (MAPTAC) shows no volume phase transition<sup>1</sup>. This seems inconsistent with the volume phase transition behavior mentioned above. For dissolving this discrepancy, a careful examination of the pH effect on the volume phase transition of NIPA-AA was carried out. We found that the volume phase transition disappeared at pH above 7.5 and appeared at pH below 6.3. The potentiometric titration revealed that the dissociation constant of carboxyl groups in NIPA-AA gel decreased with raising temperature above 34°C. The discontinuous volume change was correlated with the decrease in the carboxyl ionization of NIPA-AA gel and a significant fraction of the carboxyl group was unionized in the gel at the collapsed state. On the other hand, the continuous volume change was observed for the completely ionized NIPA-AA gel, in which all the carboxyl groups were ionized irrespective of the temperature because of high pH. The continuous volume change of NIPA-AA gel in the free salt solution was found to change to be the discontinuous one in 0.1 or 0.3 M NaCl solution. This is considered to be due to the decrease in the Donnan osmotic pressure of counter-ion in the high salt solution. In the discontinuous volume change of NIPA-AA gel at the low pH, the decrease in the ionization with raising temperature which resulted in reducing the Donnan osmotic pressure played an essential role. We conclude that the volume phase transition of NIPA gel disappears when introducing swelling Donnan osmotic pressure into the system as observed for NIPA-AA gel at the high pH. The theoretical explanation for the behavior will be also presented<sup>2</sup>.

1. S. Beltran et al J. Chem. Phys. 92, 2061(1990)

2. S. Sasaki, H. Maeda Phys. Rev. E 54, 2761(1996)

## 451.D5 A MODEL FOR LECITHIN SELF-ORGANIZATION INTO THE POLYMER-LIKE MICELLES

Yurii A. Shchipunov and Elena V. Shumilina

*Institute of Chemistry, Far East Department, Russian Academy of Sciences, 690022 Vladivostok, Russia*

Lecithin organogels consist of a three-dimensional network of entangled polymer-like reverse micellar aggregates. Their formation is promoted by addition of trace amounts of water into a nonaqueous solution containing the dissolved phospholipid. The water causes the progressive transformation of the initial spherical micelles into extremely extended tubular ones. From this fact it is apparent that the polar additive should be an essential constituent of the lecithin organogels. Nevertheless, the role of polar solvent in micellar shape transformation is poorly understood. This study was aimed at elucidating the nature of interactions of lecithin with both water and various polar solvents. In addition, the gel-forming properties of closest lecithin homologue - phosphatidylethanolamine (PE) - and mixtures of both of these phospholipids were examined. As we expected, it provided an insight into the structural organization of the polymer-like phospholipid micelles at the molecular level.

It was ascertained in the first stage that the jellification of lecithin solutions is induced not only by water but also by glycerol, formamide and ethylene glycol. Their comparison with structurally related polar organic solvents, which do not have the ability exhibiting the thickening effect, showed the gel-forming agents to be most polar than their non-gel-forming homologues and prone to create three-dimensional network from hydrogen bonds. PE formed only tubular micelles in the absence of polar solvents. Its influence on the jellification in lecithin solutions was investigated. Examination of the interactions of solvents and PE with lecithin by means of IR and <sup>31</sup>P NMR spectroscopy made it apparent that (i) molecules

of the gel-forming additives are attached to the phospholipid phosphate group, (ii) they are linked to each other via hydrogen bonds, (iii) the non-gel-forming solvents are loosely hydrogen-bonded with phosphate group and (iv) the amino group of a PE molecule forms a hydrogen bond with the neighboring lecithin molecule.

On the basis of the data obtained, a model for the tubular reverse micelles was suggested. Under this model, the polar solvents favor the self-organization of lecithin into polymer-like aggregates if they are capable of bridging neighboring phospholipid molecules. They provide the formation of an extensive ribbon-like hydrogen bonding network that consists of alternate solvent molecules and phosphate groups of lecithin.

## 452.D5

### INTELLIGENT CRYSTALLINE COLLOIDAL ARRAYS FOR OPTICAL LIMITING

Jesse M. Weissman and Sanford A. Asher

*Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, USA*

Dyed, monodisperse poly(N-isopropylacrylamide) (PNIPAM) colloids self-assemble to form a colloidal crystal which functions as an optical limiting device. The colloidal crystal transmits nearly all visible light under normal conditions, but rejects intense laser sources at a wavelength predetermined by the lattice spacing of the colloidal crystal.

PNIPAM is a temperature-sensitive polymer which undergoes a reversible volume phase transition from a swollen to a compact state when heated above its lower critical solution temperature of approximately 32 °C. The PNIPAM colloids shrink from a diameter of ~ 300 nm at 10 °C to ~ 90 nm at 40 °C. Colloidal crystals of PNIPAM colloids diffract light weakly at low temperatures and efficiently at higher temperatures because of refractive index changes of the colloids associated with the polymer phase transition<sup>1</sup>. The dyed PNIPAM colloids self-assemble because of mutual electrostatic repulsions to form an ordered array which Bragg diffracts visible light. The colloidal crystals are fabricated such the Bragg diffraction wavelength lies within the dye absorption band. At low incident laser powers not enough heat is generated to induce the polymer phase transition, but as the incident laser power is increased, the degree of heating increases and the colloidal particles become compact. The heated array rejects nearly all light meeting the Bragg condition. These materials may have applications in optical switching and flat panel display devices.

1. J.M.Weissman *et al*, *Science*, 274, 959(1996).

## 453.D5 LIGHT SCATTERING STUDY OF THE STRUCTURE OF AGAROSE GELS

A. M. Zhivkov and S. P. Stoylov

*Institute of Physical Chemistry, Bulgarian Academy of Science, 1113 Sofia, Bulgaria*

The investigation of the structure of agarose gels is of key importance for the elucidation of the mechanism of the gel electrophoresis and particularly of the pulse gel electrophoresis of DNA. The structural heterogeneity of the gel is studied both by spectroturbidimetry and the angular dependence of the intensity of the scattered light. A great increase in light scattering intensity is found for the sol-gel transition in aqueous medium. It is suggested that this is due to the creation of scattering centres where the agarose macromolecules are densely packed. The dimensions of the scattering centres are determined by the turbidity wavelength dependence and the angular dependence of the intensity of scattered light. Their refraction index is determined from the measurement of the light scattering intensity in media of different saccharose concentration. The number of the scattering centres in a unity volume and their average density is determined from the turbidity at fixed wavelength. The changes of the dimensions and the average distance between the scattering centres from the agarose concentrations are studied. On the bases of these results a model of agarose gel is suggested which contains knots, composed of aggregates of densely packed agarose molecules, connected with strings of agarose molecules.

This study was realized with the financial help of the Contract European Commission - ERB GENE CT 930024/ERB CIPDCT 940402.

## 454.E1 THE BEHAVIOR OF NONIONIC AND IONIC SURFACTANTS IN THEIR MIXED MICELLE

Hideo Akisada

*Department of Environmental Chemistry, Faculty of Engineering, Kyushu Kyoritsu University,  
Yahatanishi-ku Kitakyushu 807, Japan*

The behaviors of surfactants and counterion in mixed micelles is investigated by several methods. The binding degree of the counterion in the micelle is measured by two methods. One is electromotive force measurement by the electrode of the counterion. The binding degree of this method is constant above a mole fraction of the cationic surfactant. The other is the calculation on thermodynamical consideration that CMC of an ionic surfactant with a nonionic surfactant depends on counterion concentration and the dependence gives the binding degree of the counterion and the micellar composition. The two method does not agree in low composition of the ionic surfactant. It is presumed that the latter includes the counterion in a part of the diffused layer moving with the micelle.

When a surfactant has optical activity, circular dichroism (CD) is an effective method for observation of environment around the head group of the surfactant. The optical active surfactant, MEG-10 is affected by mixing ionic surfactant on CD. The effects of cationic and anionic surfactants showed different behavior on CD. The CD linearly changed with the anionic surfactant concentration. However, it became constant above 0.25 mole fraction of the cationic surfactant. The binding degree became constant above 0.7 mole fraction of the cationic surfactant.

Experimental: The nonionic surfactants used were decyldimethylphosphine oxide, dodecyldimethylphosphine oxide and MEG-10. The cationic surfactants were dodecyltrimethylammonium bromide and octadecyltrimethylammonium chloride. The anionic surfactant was sodium dodecanesulfonate. A commercial electrode was used for the measurements of concentration of chlorine ion. The CMCs of a ionic surfactant with a nonionic surfactant and a counterion salt were decided by differential conductivity method.

## 455.E1 OSMOTIC PRESSURE OF AQUEOUS SOLUTIONS OF TRITON X100

V.L. Alexeev, G.A. Evmenenko

*Petersburg Nuclear Physics Institute, 188350, Gatchina, Russia*

It has been recently shown [1] that the compatibility of aqueous mixtures containing hydrophylic mineral particles such as silica and nonionic surfactants such as Triton X100 or  $C_{12}E_4$  substantially depends on the water content. Compatibility was obtained only when the water content was sufficient to fully hydrate the oxyethylene chains of the surfactants, thereby avoiding competition between silica and surfactants for the available water. This competition for water is a key to the stability of multicomponent aqueous mixtures. Indeed, each component in the mixture has its own affinity for water, which is expressed by an equation of state, i.e. the curve of osmotic pressure vs. volume fraction. When the osmotic pressure difference between components is large, the component with the higher pressure will extract water from the others, causing them to aggregate. Thus, the knowledge of osmotic pressure of the components is an essential ingredient of our understanding the conditions which make possible the compatibility.

For this aim we measured the osmotic pressure of aqueous solutions of Triton X100 in concentration range from 20 to 98 w% using osmotic stress technique pioneered by Parsegian V.A. et al. [2]. Experimental results are fit by the relation:  $\log_{10} \Pi = 4.33 + 0.81e^{0.015c}$ , where  $\Pi$  is the osmotic pressure in Pascal,  $c$  is the weight percent of Triton X100. In the form of virial expansion the fitting gives the following relation:  $\Pi$  (Pa) =  $0.094 + 36.782 X - 66.179 X^2 + 39.09 X^3$ , where  $X$  is the mass fraction of Triton. In such representation the equation of state for Triton X100 clearly demonstrates three different ranges of osmotic pressure behaviour similar with early obtained data for silica particles [1]. For application we recommend to use the first kind of fitting. The empirical relation for osmotic pressure of Triton X100 may be useful in all cases where the knowledge of osmotic pressure is an essential ingredient of understanding the processes in which Triton X100 plays a major role.

1. V.L. Alexeev et al. *Langmuir*, 1996, 12, 2392.

2. V.A. Parsegian et al. In *Methods in Enzymology*; Packer L., Ed., Academic Press:N.Y., 1986, v.127, 400

**456.E1 STUDY ON SURFACTANT SOLUTIONS BY HIGH PRECISION CALORIMETRY****Makoto Aratono<sup>1</sup>, Akoi Ohta<sup>1</sup>, Norihiro Ikeda<sup>2</sup>, Kinsi Motomura<sup>1</sup> and Takanori Takiue<sup>1</sup>**<sup>1</sup>*Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812-81, Japan*<sup>2</sup>*Faculty of Human Environmental Science, Fukuoka Women's University, Fukuoka 813, Japan*

The enthalpy of mixing water and polyethyleneglycol mono-octyl ether [ $C_8H_{17}(OC_2H_4)_jOH$ ,  $C_8E_j$ ] was measured precisely for  $j=3,4$ , and  $5$  as a function of concentration of the surfactant and temperature by using the high accuracy isothermal titration calorimeter, Thermal Activity Monitor TAM. The differential enthalpies of solution of monomer and micelle, the partial molar enthalpy change of  $C_8E_j$  and that of water of micelle formation, and the heat capacity changes were evaluated by applying the thermodynamic relations to the enthalpy of mixing.

It was shown that the dissolution of pure liquid  $C_8E_j$  is exothermic and the value of the enthalpy mixing decreases with increasing the concentration of the solution and with lowering the temperature. The differential enthalpy of solution of pure liquid  $C_8E_j$  into water as monomer is negative and increasing with increasing temperature. This suggests that there is stronger interaction between water and monomeric  $C_8E_j$  molecules and the interaction is significantly dependent on temperature. The differential enthalpy of solution of  $C_8E_j$  molecules and the interaction is significantly dependent on temperature. The differential enthalpy of solution of  $C_8E_j$  into water as micelle particles was less negative compared with the one as monomer. Therefore, the micelle formation is endothermic from the viewpoint of the partial molar enthalpy change of surfactant molecules. However, the experiments and thermodynamic analysis suggested that the micelle formation is exothermic from the point of view of the differential enthalpy of dilution of water. The heat of mixing of  $H(OC_2H_4)_jOH$  were also measured and the differential enthalpies of solution were evaluated. It will be shown that the results are useful to shed light on the role of hydrophilic group of  $C_8E_j$  in the dissolution process.

The change in the heat capacity, accompanied by the dissolution and micellization processes were also calculated from the temperature dependence of the enthalpies. The partial molar heat capacity change vs molality curves for  $C_8E_j$  and that for water were found to have a sharp maximum or minimum and both its height and width are strongly temperature dependent.

Furthermore, the thermodynamic equations were developed based on the idea that the thermodynamic quantities of a micelle particle are defined by excess ones with respect to an appropriate spherical dividing surface around the micelle particle. It was found that the useful information on the average aggregation number and its temperature dependence is obtained by applying these equations to the results given above.

**457.E1 EFFECT OF TERMINAL HYDROXYL GROUP AND OLOGOOXYETHYLENE CHAIN ON SURFACTANT POLARITY DETERMINED BY INVERSE GAS CHROMATOGRAPHY****J. Blaszcak, A. Voelkel and J. Szymanowski***Institute of Chemical Technology and Engineering, Poznan University of Technology, Poznan, Poland*

The polarity index of ethanol  $PI = 100\log(C-4.7)+60$ , where  $C$  is the apparent number of carbon atoms in a hypothetical  $n$ -alkane having the same retention time as ethanol and  $PI$  is the polarity index, was determined by inverse gas chromatography for model individual 1,3-di( $\omega$ -alkoxyoligo(oxyethylene)propan-2-ols, 2-[N,N-di( $\omega$ -alkyloligooxyethylene)amine]ethanol and tri( $\omega$ -alkyloligooxyethylene)amine was determined by inverse gas chromatography and correlated with the contents of hydroxyl group and oligo(oxyethylene) chain(s). The studied model compounds were used as a liquid phase in a chromatography column and retention times of ethanol and  $n$ -alkane probes were measured at standard temperature  $70^\circ C$ . The polarity index depends on the contents of the hydroxyl group and oligo(oxyethylene)chain(s) and on the distribution of oxyethylene units and alkyl groups in surfactant hydrophilic and hydrophobic moieties, respectively. The isopolarity approach permits to assess the contribution of the hydroxyl group to surfactant polarity in respect to the oxyethylene group content. 1 w/w% of the oxyethylene group is equivalent to 0.12-0.17 w/w% of the hydroxyl group.

1. J. Szymanowski, Crit. Rev. Anal. Chem., 21, 407 (1990).



**458.E1****BASIC HYDROLYSIS OF P-NITROPHENYL PENTANOATE  
IN THE PRESENCE OF CTAB MICELLES****Camelia Bobica, Dan F. Anghel and Anca Voicu***Romanian Academy, Institute of Physical Chemistry, Spl Independentei 202, 79611 Bucharest, Romania*

Hydrolysis of esters can occur through acid-catalyzed [1], pH-independent [2], and base-catalyzed [3] mechanisms. Owing to the relative simplicity of base-catalyzed carboxylic ester hydrolysis, these reactions have served well as model systems in investigations of micellar effects on reaction rates and activation parameters. In addition, the preponderance in biological systems of carboxylic esters catalyzed by nucleophiles and by enzymes makes the investigation of micelle catalyzed ester hydrolyses of obvious importance.

In a previous work we studied the alkaline hydrolyses of p-nitrophenyl acetate, propionate, and butyrate in the presence of hexadecyltrimethylammonium bromide (CTAB) micelles [4]. The present paper deals with the same hydrolysis using as substrate the p-nitrophenyl pentanoate.

In order to emphasize the effect of the micelles upon the hydrolyses, the reactions were investigated in various conditions: in the absence of micelles, in the presence of micelles, and in presence of both micelles and an added electrolyte (KBr).

The data were fitted by means of pseudo-phase ion-exchange model. The ion-exchange constant, the solubilization constant of the substrate and the micellar rate constant were obtained. They were employed for a discussion about the behavior of the pentanoate in the above mentioned series of p-nitrophenyl esters.

1. P.K. Das Gupta and S.P. Moulik, *Indian J. Chem.*, 28 A (1989) 953
2. J.M. Patel and D.E. Wurster, *Int. J. Pharm.*, 86 (1992) 43
3. R. Germani, G. Savelli, N. Spreti, G. Cerichelli, G. Mancini and C.A. Bunton, *Langmuir*, 9 (1993) 61
4. C. Bobica, D.F. Anghel and A. Voicu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 105 (1995) 305

**459.E1****INVESTIGATION OF CATIONIC SURFACTANT  
AQUEOUS SOLUTIONS BY QUASIELASTIC SLOW NEUTRON SCATTERING****L.A. Bulavin<sup>1</sup>, A.G. Mironyuk<sup>1</sup>, T.V. Karmazina<sup>2</sup>, V.I. Slisenko<sup>3</sup>, N.A. Klimenko<sup>2</sup>**<sup>1</sup>*Kiev State University, Kiev, Ukraine;*<sup>2</sup>*Institute of Colloid and Water Chemistry of National Academy of Science of Ukraine, Kiev, Ukraine*<sup>3</sup>*Institute for Nuclear Research of National Academy of Science of Ukraine, Kiev, Ukraine*

The dynamic state (the overall diffusion coefficients, the contributions from collective and single-particle motions, and lifetimes of the vibrational state) of molecules in water-cationic surfactant (dodecyl- and hexadecylpyridinium bromides, DDPB and HDPB, respectively) systems by quasielastic slow neutron scattering have been investigated. The information on the mechanism of diffusion has been obtained by Bulavin-Oskotsky model. The concentration dependencies of the water-cationic surfactant systems are similar for both homologues studied. As the concentration of cationic surfactant in water rises up to critical micelle concentration (CMC), the contribution of Lagrange or collective particles initially increases in comparison with pure water; then the contribution from the collective motions decreases due to micellization. The minimum contribution to the overall self-diffusion coefficient from the single-particle motions (the jump-wise mechanisms of diffusion) and the maximum contribution from the collective motions (the continuous mechanism of diffusion) corresponds to the CMC for both surfactants within the concentration range studied. We should note that the value of overall diffusion coefficient for the studied DDPB solution is close to the value of the overall diffusion coefficient of the molecules in pure water. The overall diffusion coefficient decreases with the increasing alkyl chain length, mainly because the jump mechanism of diffusion becomes less important. Deviation of the dynamic state of the water-surfactant system from corresponding characteristics of water becomes more pronounced with increasing length of alkyl radical in the molecule of cationic surfactant. As concentration of surfactant increases after CMC, the contribution to the overall diffusion coefficient from collective motions of molecules decreases and the single-particle motions become more important. The contribution from a -CH<sub>2</sub>-group to change the

characteristic of dynamic state of water is quantitatively estimated. Determination of the increments is arbitrary, however, permit us to estimate the characteristics of dynamic state, for example for decyl- and tridecylpyridinium bromide and other solutions without performing experiments. The increments per  $-\text{CH}_2-$  group at CMC: for overall diffusion coefficient:  $-0.05 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ; the contribution from the single-particle:  $-0.033 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ ; collective motions:  $-0.025 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and the lifetime of the vibrational of molecules  $-0.0088 \times 10^{-12} \text{ s}$ . The characteristics of dynamic state are evaluated with an error determined by the energy resolution of the setup and no more then 8%.

## 460.E1 PHASE BEHAVIOR OF CTAB/1,6-HEXANEDIOL/WATER SYSTEM

Olga Cañadas, Mercedes Valiente, Elvira Rodenas

*Dpto. Química Física, Universidad de Alcalá, E-28871 Madrid, Spain*

Many phase diagrams of ternary surfactant/alkanol/water systems have been studied. On the contrary, ternary systems with diols have been less studied. In this communication, we present the phase diagram of the ternary CTAB/1,6-hexanediol/water system. The system shows a wide isotropic region from the water corner to 8 % wt. water content and two liquid crystal phases. The phase diagram is analyzed in comparison with the CTAB/hexanol/water phase diagram showing the micellar region is much larger than in hexanol system. This region has been studied by conductivity and fluorescence measurements. The influence of the micelles on the basic hydrolysis of Crystal Violet has also been studied.

## 461.E1 MIXED MICELLES OF CTAB AND $\text{C}_{12}\text{E}_4$ SURFACTANTS

M<sup>a</sup> del Sol Villafuela, Mercedes Valiente, Elvira Rodenas

*Dpto. Química Física Universidad de Alcalá E-28871 Madrid, Spain*

Mixed micelles of cetyltrimethylammonium bromide (CTAB) and dodecyltetraethylenglicol ( $\text{C}_{12}\text{E}_4$ ) have been studied by surface tension, conductivity and fluorescence measurements. The CMC values, determined by surface tension measurements, decrease with the molar fraction of the nonionic surfactant and these CMC values are always smaller than the ones calculated from ideal behavior. The conductivity study suggests that two kinds of micelles exist in aqueous solution. The shape of the mixed micelles changes from spherical to non-spherical micelles depending on the surfactant composition and concentration as we can deduce from the aggregation numbers.

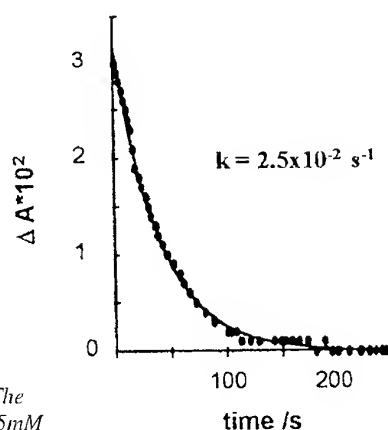
## 462.E1 PHOTOEXCITED FULLERENE SPECIES IN MICELLES

Julian Eastoe<sup>1</sup>, Esther R. Crooks<sup>1</sup> and Andrew Beeby<sup>2</sup>

<sup>1</sup>*University of Bristol, England*

<sup>2</sup>*Univarsity of Durham, England*

Fullerene  $\text{C}_{60}$  may be incorporated into Triton X100 micelles to give stable aqueous solutions and this allows photoexcited states to be stabilised. Of particular interest is the radical anion  $\text{C}_{60}^-$  which can have a lifetime  $t$  of up to 5 minutes here. Mechanistic studies, using laser flash photolysis and NIR spectroscopy, show that  $\text{C}_{60}^-$  can be formed in the presence of an electron donor via the triplet state  $^3\text{C}_{60}$ . Small-angle neutron scattering (SANS) and stopped-flow spectrophotometry have also been used to find out about structure and micelle lifetimes in these systems. A mechanism consistent with these findings for  $\text{C}_{60}^-$  formation/decay is proposed.



*Decay of  $\text{C}_{60}^-$  monitored at 1077nm. The solution contains 2% TX100-R with 2.5mM sodiumascorbate.*

## 463.E1 EVALUATION OF THE PARTITION COEFFICIENT OF SURFACTANTS IN LIQUID-LIQUID SYSTEMS

M. Ferrari<sup>1</sup>, L. Liggieri<sup>1</sup>, F. Ravera<sup>1</sup>, R. Miller<sup>2</sup> and A. Passerone<sup>1</sup>

<sup>1</sup>*Istituto di Chimica Fisica Applicata dei Materiali -CNR, Genova, Italy*

<sup>2</sup>*Max Plank Institut für Kolloid und Grenzflächenforschung, Berlin, Germany*

An experimental technique to evaluate the partition coefficients is presented here applicable to liquid-liquid systems in which a surfactant solute is dissolved. This method is based on the measurement of the surface tension of the aqueous surfactant solution after the equilibration with the other liquid phase.

Experimental data have been obtained for some n-alkyl dimethyl phosphine oxides ( $C_n$ DMPO), octylphenyl polyethylene glycol ethers (Triton X-100 and Triton X-405), and one polyoxyethylene cetyl ether ( $C_{16}E_{20}$ ).

These results show that at monomeric concentrations, most of the surfactant used have a non zero value of the partition coefficient. These results are particularly important when adsorption processes at liquid-liquid interfaces are under consideration.

## 464.E1 INTERMEDIATE STRUCTURES IN AMPHIPHILIC/WATER SYSTEMS

Sérgio S. Funari<sup>1</sup> and Gert Rapp<sup>2</sup>

<sup>1</sup>*MPI-Colloids and Surfaces, Teltow, Germany, correspondence address: EMBL.....*

<sup>2</sup>*European Molecular Biology Lab., Outstation Hamburg, Notkestr. 85, 22603 Hamburg*

We have measured time-resolved X-ray diffraction in the  $C_{16}EO_6$ /water system on heating and cooling scans. Different phases were observed and their structure determined. Between hexagonal and lamellar phases the structure is dependent of the thermal path. Heating from hexagonal forms a cubic while cooling from lamellar leads to an intermediate phase.

Amphiphilic molecules normally have long hydrophobic alkyl chains attached to a hydrophilic polar group. The so-called hydrophobic effect forces these molecules to self aggregate forming mesogenic units, or micelles. Amphiphilic bilayers are simple models for cell membranes. This association is valid because the hydrophobic effect is the common driving force for their aggregation and their properties are similar

Aqueous dispersions of  $C_nEO_m$  with long alkyl chains can form intermediate phases. In many cases their structures resembles one of their neighbour phases and data from them can be misinterpreted. So far, they have been assigned as disrupted lamellar in  $(C_{16}EO_6)$ <sup>1</sup> and  $C_{22}EO_6$ <sup>2</sup> and rhomboedral in the  $C_{30}EO_9$ <sup>3</sup> systems.

A sample with 54 wt%, showed at room temperature a hexagonal phase,  $a = 6.69$  nm. Heating the system leads to a Ia3d cubic phase with  $a = 14.2$  nm. Further heating reaches a lamellar phase with interplanar distance  $d = 5.70$  nm.

A time-resolved sequence of diffraction patterns taken on cooling, Fig. 1, clearly shows that both lamellar and intermediate structures have a common repeat distance corresponding to  $s = 1/5.70 = 0.175$  nm<sup>-1</sup>, a necessary condition for an epitaxial relationship between these phases. The analysis of the peaks at this  $s$  value shows a significant increase in intensity once the transition from lamellar to the intermediate takes place. The peak intensity decreases again after the transition to the hexagonal phase, confirming that this scattering plane is present in both lamellar and intermediate phases.

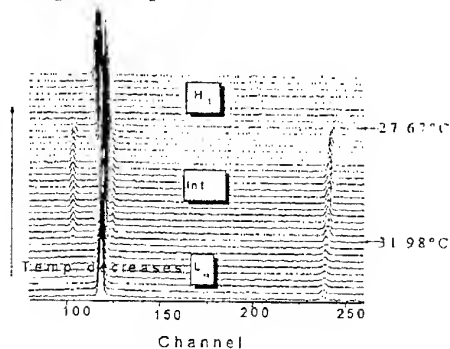


Fig. 1. Time resolved SAXS of 54 wt%  $C_{16}EO_6$  in water, collected on a cooling scan. The phase sequence  $L_n$  to intermediate to hexagonal  $H_1$  and the respective temperatures of the phase transitions can be seen.

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2. Funari S.S., M.C. Holmes and G.J.T. Tiddy. 1992., *J Phys. Chem.* 96:11029-11038.
3. Burgoyne J., Holmes M.C. and Tiddy G.J.T., *J. Phys Chem.*, 99(16), 6054 (1995).

## 465.E1

X-RAY STUDIES ON THE C<sub>12</sub>EO<sub>2</sub>/WATER SYSTEMSérgio S. Funari<sup>1</sup> and Gert Rapp<sup>2</sup><sup>1</sup>MPI-Colloids and Surfaces, Teltow, Germany<sup>2</sup>EMBL-Outstation Hamburg, Notkestrasse 85, D-22603 Hamburg, Germany

We investigated the C<sub>12</sub>EO<sub>2</sub>/water system aiming to determine the structural parameters of the lamellar and cubic phases (1). Two neighbouring cubic phases were seen and the transition between them was temperature, but not concentration, driven. At temperatures near the cloudy point the equilibrium conditions are difficult to be reached, leading to the formation of cubic phases with apparently the same structure but distinct thermal behaviour. One being insensitive to temperature changes while the other seemed to shrink with heating, Fig. 1.

Time-resolved diffraction patterns were recorded on heating and cooling scans. Analysis of our data showed that the chosen rates were not sufficient to follow the system in equilibrium conditions. However the peaks observed were enough to allow a secure identification of the structures. Some patterns were collected using a 2D detector at constant temperatures. The Ia3d showed 6 peaks with corresponding spacing ratios of  $\sqrt{6}:\sqrt{8}:\sqrt{14}:\sqrt{16}:\sqrt{20}:\sqrt{22}$ , and the Pn3m 4 peaks:  $\sqrt{2}:\sqrt{3}:\sqrt{4}:\sqrt{6}$ .

The parameters of the lamellar phase were concentration dependent (2), showing repeat distances around 5 nm, which corresponds to thickness of the hydrocarbon core of 2 nm and a head group thickness of about  $d_{eo} \sim 1$  nm.

The cubic phases have been identified as Ia3d (lower temperatures) and Pn3m (higher temperatures). The Ia3d found in a sample with 67 wt% showed a lattice parameter  $a = 12.9$  nm, length and radius of the rods  $l = 4.5$  nm,  $r = 2.5$  nm respectively. The same parameter for the Pn3m phase were  $a = 12.2$  nm,  $l = 4.3$  nm and  $r = 2.7$  nm.

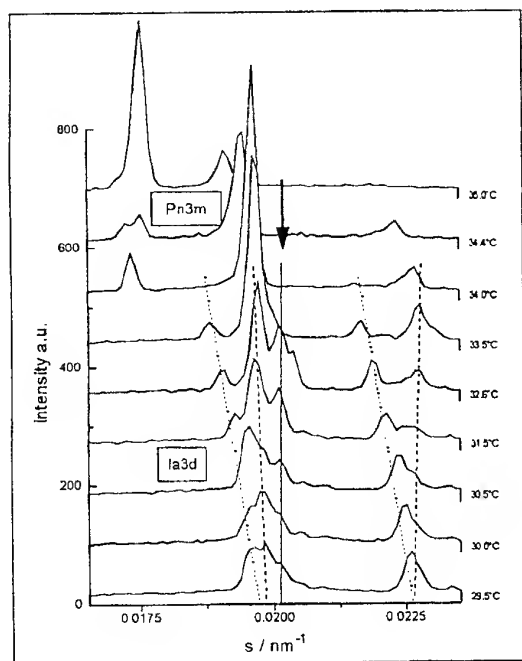


Fig. 1. Time resolved diffraction pattern of the 70 wt % C<sub>12</sub>EO<sub>2</sub>/water sample. At low temperatures one sees two cubic phases compatible with Ia3d space group (dashed lines) showing two reflections for each of them and peaks of an unidentified phase (solid line corresponding to  $d=5.0$  nm), indicated by the arrow. At higher temperatures another cubic phase is seen and has been attributed the Pn3m space group.

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2. Funari S.S. and G. Rapp. *J Phys. Chem.*, in press.

## 466.E1 MARKOV CHAIN MODEL OF MIXED SURFACTANT SYSTEMS

G. S. Georgiev

*University of Sofia, Faculty of Chemistry, 1 J. Bourchier Avenue, 1126 Sofia, Bulgaria*

The polydispesity of commercial surfactants, synergetic behaviour of mixed surfactant systems and the possibility to control their physical properties and stability by a variation of the surfactant composition are the reason for a growing applied interest in these systems. In addition functional molecular aggregates in nature are composed of two or more kinds of surface-active chemical species. Therefore, the studies of mixed micelles, mixed films or mixed surfactant phase organization are essential not only for developing the surfactant abilities in the applied aspect, but also for comprehending some functions of biological systems. This situation has led to an enormous challenge to understand the interaction mechanism between different components in the mixed surfactant systems. From the first pseudo-phase separation model the mixed surfactant system simulation passes through the ideal-mixed formation model and came to the non-ideal one.

A new model of mixed surfactant systems have been developed in the work presented. It includes two parameters ( $g_i$ ,  $i=1,2$ ) only connected directly with the Gibbs free energy of the equilibrium surfactant aggregation reactions

$$g_i = \exp[-(\Delta G_{ii}^0 - dG_{ij}^0)/RT]; \quad i,j = 1,2; \quad i \neq j$$

They can be determined using both the aggregation equilibrium constant values of the phase composition data. It has been shown also the relation between these new parameters and the same of the regular solution approximation and the alternative models. The possibility to describe the available experimental information about the micelle composition as a function of the singly dispersed surfactant mixture composition, better than other models, has been shown also.

## 467.E1 KRAFFT POINTS OF ALKYL SULPHATES: DIFFERENT EFFECT OF LOWER AND HIGHER ALIPHATIC ALCOHOLS

Germasheva I.I., Bitjutskaia L.A.

*NPAO "SintezPAV", Voronezh University, Russia*

Using the method of polythermal polyconcentration conductometry, the Krafft point parameters of alkyl sulphate solutions have been studied in the presence of lower ( $C_2$ - $C_7$ ) and higher ( $C_{10}$ - $C_{16}$ ) aliphatic alcohols. Higher alcohols exhibit a complexing effect, i.e. they form the complex "alkyl-sulphate-alcohol" which possesses surface-active properties; the solution here should be considered as a solution of a mixture of two surfactants. The data have been interpreted in terms of the strict thermodynamical theory of surfactants behavior on the Krafft boundary using the two-phase Van der Waals equation (A.I. Rusanov). Typical for lower alcohols is a desaggregating effect - the initially existing alkylsulphate micelles desaggregate in an aqueous or alcoholic solution on addition of alcohol or water, respectively, up to the region where there is practically no micelle formation with rising CMC and decreasing Krafft temperature with subsequent formation of micelles having a new structure - alcoholic or aqueous, respectively. Thermodynamical factors are discussed. The conductivity polytherm can be a criterion for the purity of surfactants, being more informative than the known surface tension criterion and allowing not only to detect the impurity but also to determine its nature and to define the separation conditions.

## 468.E1 HYDROTROPY, HYDROTROPES AND HYDROTROPIC EFFECT IN NONIONIC AMPHIPHILES

Gaspar González<sup>1</sup> and M. Elizabete D. Zaniquelli<sup>2</sup>

<sup>1</sup>*Petrobras Research and Development Center Cidade Universitária Quadra 7, Ilha do Fundão, Rio de Janeiro, Brazil*

<sup>2</sup>*Depto. De Química e Letras, Universidade de São Paulo, Ribeirão Preto, Brazil*

Hydrotropy is a name used to designate the enhancement in the aqueous solubility of poorly soluble organic compounds caused by the addition of other type of amphiphiles called hydrotropes or hydrotropic

agents. Anionic organic salts like sodium benzoate and hydroxybenzoates, salicylates, benzene-, toluene-, xylene- or naphthalenesulfonate as well as the cationic compound p-aminobenzoic acid-hydrochloride and nonionics like pyrogallol, cathecol and resorcinol are reported to present hydrotropic properties.

Although hydrotropy is extensively used in industry, the molecular mechanism of hydrotropic solubilization has not been completely elucidated yet. In this paper we examine the interaction between a nonionic surfactant (ethoxylated fatty alcohol containing between five and six oxyethylenic units) and sodium p-toluene sulfonate. Surface tension measurements confirm that the hydrotropic effect occurs at a concentration in which the hydrotrope self-associate. Photon correlation spectroscopy studies show that for this concentration of hydrotrope a drastic reduction the surfactant micellar radius occurs. Furthermore the luminescence of the hydrotrope used as a fluorescence probe indicate that at low concentrations p-toluene sulfonate dissolves in the surfactant micelles but beyond the minimum concentration for hydrotropic solubilization, the hydrotrope is present in the aqueous phase. These results suggest that the hydrotropic effect is related to alterations in the water structure induced by the hydrotrope molecules.

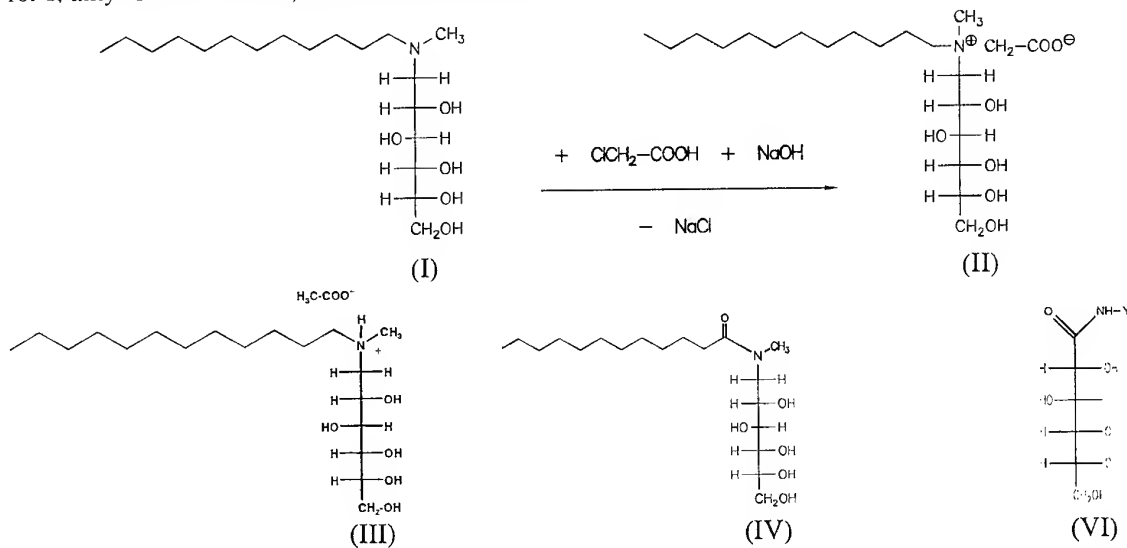
## 469.E1 NOVEL SURFACTANTS DERIVED FROM AMINO SUGARS - SYNTHESIS AND SURFACE CHEMICAL PROPERTIES IN CORRELATION WITH THE STRUCTURE

Klaus Haage

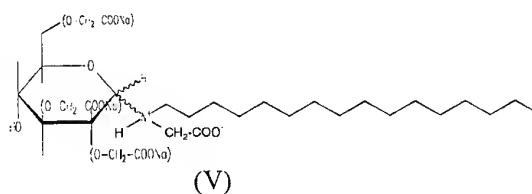
Max-Planck-Institute for Colloids and Interfaces, Department of Interfaces, Berlin-Adlershof, Germany

In colloid and interface science the influence of adsorption layers of amphiphiles on the properties of fluid surfaces is tremendously important, it is caused by the orientation of molecules, based on their structure. We investigated the correlation between different surface chemical properties, like interfacial tension lowering, foaming ability, viscosity e.g., and the structure of selected surfactants, derived from amino sugars.

Nowadays nonionic carbohydrate amphiphiles are of increasing interest and on the other hand ampholytic surfactants possess strong interactions to solid surfaces and to other amphiphiles. We synthesised combinations of different hydrophilic groups, like betaine structure at hexoses (II), derived from alkyl glucamines (I), and we compared the properties with the simple basic structures (alkyldimethyl amine salts for I; alkyl betaines for II) and with the salts (III).



Further comparisons were made with the analogous acyl compounds (IV) and mixtures of multicarboxymethylated glycosyl amines, like (V) for ex., the products of carboxymethylation of glycosyl amines. The latter are condensation products of fatty amines and glucose. The reaction of different amino compounds with D-glucono-



lactone resulted in amido compounds (VI) of lower solubility, so that the combination with stronger hydrophobic amino acids yields surface activity [ $Y = \text{CH(R)}\text{-COONa}$ ].

To characterise the influence of the different groups we measured the adsorption isotherms for the surface and interfacial tension of the homologous pure model compounds and fitted it with the Frumkin equation. The hydrophilic power of the polyol structures could be specified.

## 470.E1 NOVEL SURFACTANT SPECIES DEVELOPED IN THE MOLECULAR COMPLEX FORMATION SYSTEMS COMPOSED OF SURFACTANTS AND ADDITIVES

Hiroataka Hirata, and Nahoko Iimura

Niigata College of Pharmacy, 2-13-5 Kamishin'eicho Niigata, 950-21 Japan

In these few years we have succeeded in the stable isolation of many kinds of crystalline molecular complexes between surfactants and various additives. They are, of course, composed in a definite molar ratio as shown Table 1. To date we have also obtained abundant structural knowledge of the surfactant complexes by X-ray analysis. Some typical structures are presented in Figure 1. Thus we have been able to firmly establish the presence of such complexes as new chemical species. Moreover, it has been clarified that the stably isolated surfactant molecular complexes, treated in the solution systems, behave themselves to be new surfactant species, e.g., showing their own characteristic cmcs and inherent Krafft points different from their mothers'. The complex species also satisfied the well-known linear relationship of  $\log \text{CMC}$  vs. carbon numbers of surfactant alkyl chains as illustrated in Figure 2 where each species homologically represented different slopes from each other and from the mother series. The fact distinctly designates that the complex species derived from a mother surfactant are another different surfactant species in nature like daughters. The crystalline surfactant molecular complexes which are yielded from aqueously treated conventional solubilized solution systems at cool condition are, on warming, instantaneously dissolved and promptly realize the original solubilization systems again, of course, restoring all the solution characteristics. It strongly suggests that the phenomenon so far referred to as "solubilization" is not special but just a common one like daily observable dissolution of any crystalline salt.

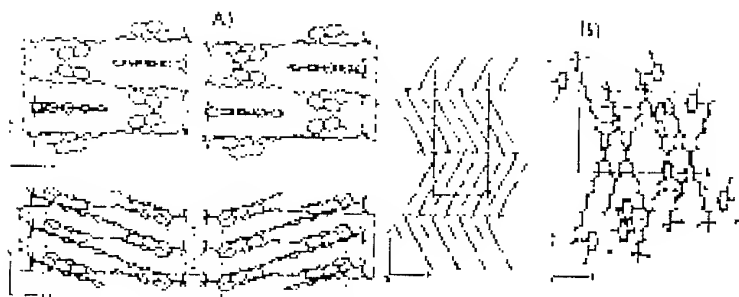


Figure 1. Crystal packings of the anionic and the cationic surfactant molecular complexes on each projection, A) sodium octyl sulfate/2-naphthol and B) CTAB/o-iodophenol, respectively

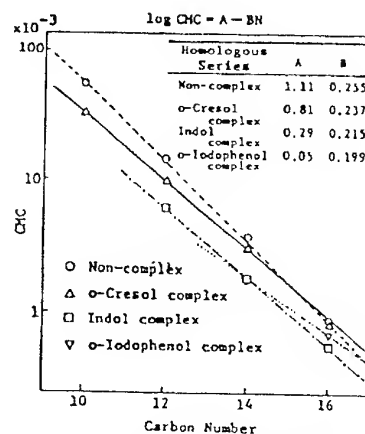


Figure 2. Plots of  $\log \text{CMC}$  vs. C-numbers

Table 1. Some typical data of the surfactant molecular complexes

Complex species (Surfactant/Additive)	Molar composition (Surfactant/Additive)	cmc (mmol/dm <sup>3</sup> )	Krafft point (°C)
CTAB/o-iodophenol	1/1	0.70	22.6
/2-naphthol	1/1	0.60	22.7
/a-naphthylamine	2/1	0.42	24.0
/diphenylamine	2/1	0.57	35.3
SLS/p-iodophenol	3/2	4.00	0.4
/2-naphthol	3/2	4.00	5.3
SMS/p-iodophenol	3/2	1.31	1.0

**471.E1****MIXED MICELLE FORMATION IN SOLUTIONS  
OF NONIONIC AND CATIONIC SURFACTANTS****Ivanova N.I., Grishutin S.G.***Colloid Chem. Dept., Chem. Faculty, M.V. Lomonosov Moscow State University, 119899 Moscow, Russia.*

The surface adsorption and micelle formation in two systems: of Triton X-100 (ethoxylated isooctyl phenyl with average polyethylene oxide chain length of 9,5) - CTAB(cetyltrimethylammonium bromide) and Triton X-100 - CPB (cetylpyridine bromide) in aqueous  $10^{-3}$  M KBr solutions was investigated by the surface tension measurement. It was shown that the negative deviation of CMC in mixed solutions from values CMC for ideal surfactant mixture are observed in both systems. The deviation is largest in Triton X-100 - CTAB system. The absolute values of molecular interaction parameters in the micelles ( $\beta_m$ ) and in the surface layers ( $\beta_s$ ) was calculated. The interaction in mixed micelles is much weaker than in mixed monolayers at the air/aqueous solution interface. The mole fraction of nonionic surfactant in mixed micelles and mixed adsorption layers is largest than the mole fraction of nonionic surfactant in the total surfactant in the solution phase.

**472.E1****TITRATION AND FLOW CALORIMETRIC INVESTIGATIONS OF THE  
AGGREGATION AND ADSORPTION OF NONIONIC SURFACTANTS****Z. Király\*, R.H.K. Börner and G.H. Findenegg***Technical University of Berlin, Iwan-N.-Stranski-Institute of Physical and Theoretical Chemistry,  
Strasse des 17. Juni 112, 10623 Berlin, Germany**\*on leave from: Department of Colloid Chemistry, Attila Josef University, Aradi Vt. 1,  
H-6720 Szeged, Hungary*

The critical micelle concentrations and the enthalpies of micelle formation of n-octyl tetraoxyethylene glycol monoether ( $C_8E_4$ ) and n-octyl- $\beta$ -D-monoglucoside ( $C_8G_1$ ) in water have been determined at 298.15 K by titration microcalorimetry. The adsorption and thermal behaviour of these nonionic surfactants at the hydrophilic silica glass/aqueous solution interface have been investigated by simultaneous measurements of the adsorption isotherm and the calorimetric enthalpies of displacement in a flow system. Both surfactants display pronounced cooperative adsorption behaviour (S-shaped isotherms). While in the low affinity region, the amount adsorbed and the integral enthalpies of displacement are only slightly smaller for  $C_8G_1$  than for  $C_8E_4$ , the deviation increases to one order of magnitude in the aggregative adsorption region. The observed difference in the adsorption behaviour is interpreted in terms of the different hydrophilic headgroups of the two amphiphiles. The differential enthalpies of displacement are comparable in magnitude in both the low affinity (exotherm) and aggregative (endotherm) regimes. The molar enthalpies of aggregate formation at the silica/water interface were found to be close to those in the bulk solution indicating that surface aggregation and bulk micellization are very similar phenomena. The thermodynamic potential functions of the formation of the adsorption layer indicate a delicate balance between the large entropy and enthalpy terms resulting in a moderate decrease in the Gibbs free energy.

**473.E1****RAYLEIGH SCATTERING MEASUREMENTS ON A  
LYOTROPIC CALAMITIC NEMATIC LIQUID CRYSTAL PHASE:  
THE BACKFLOW PROBLEM REVISITED****M.B. Lacerda Santos and M.A. Amato***Departamento de Física, Universidade de Brasília 70910-900 Brasília, DF, Brazil*

Using a light-beating technique we have measured the damping time of thermal fluctuations of the nematic director for the so called cylindrical or calamitic nematic phase  $N_c$  of the lyotropic system K-laurate/decanol/  $D_2O$ . The relative concentrations were chosen in order to have a large temperature range for the  $N_c$  phase, so the measurements were performed far from any phase transitions. By varying the scattering



angle in suitable geometries, it was then possible to estimate the orientational diffusivities (ie, ratios between elastic and viscosity constants) associated to the three pure deformations of splay, twist and bend. A former measurement<sup>2</sup> in a similar system exhibiting the disk-like  $N_D$  phase yielded a large deviation between the splay and twist diffusivities. This effect was then interpreted in terms of induced flows, or back flow, a mechanism formerly used to explain the reduction in the bend viscosity for classical rod-like nematics<sup>2</sup>. However, in the case of the  $N_D$  phase of Ref.[1] it was argued that an important reduction of the splay viscosity could take place thanks to an interchange of the role played by disks and rods in the two types of phases.

The new measurements reported here allow to discuss more fully the applicability of the backflow mechanism to a nematic system made up of micelles, mesoscopic objects whose shape in the  $N_C$  phase is expected to be nearly cylindrical. The results are consistent with this view, and confirm the interchange effect mentioned above.

1. M.B. Lacerda Santos, Y. Galerne and G. Durand, 1985, J. Phys., Paris, 46, 933.

2. Orsay Liquid Crystal Group, 1971, Mol. Cryst. Liq. Cryst. 13, 187.

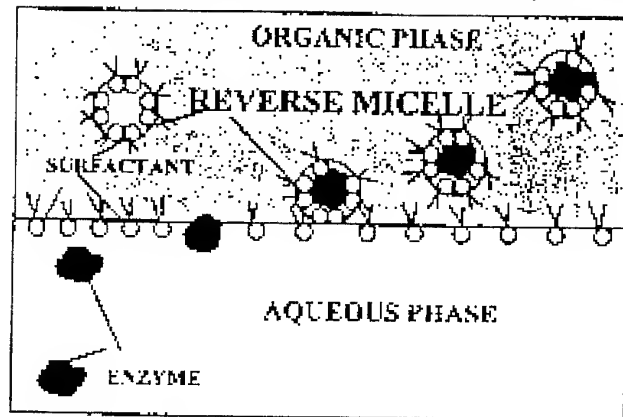
## 474.E1

### APPLICATION OF SURFACTANT-CONTAINING ORGANIC SOLVENTS IN THE EXTRACTION OF ENZYMES

Z. Lazarova, K. Tonova, V. Dimitrova,

*Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

In recent years, increased attention has been given to the development of efficient methods for separation, concentration, and purification of proteins and other bioproducts from fermentation and cell culture media. One of the most promising methods is the Reversed Micellar Liquid-Liquid Extraction. The organic solution contains in this case an ionic surfactant. The submicroscopic aggregates (10-100 nm) of surfactant molecules enable the uptake of water and hydrophilic protein molecules from the aqueous into the organic phase. The mechanism is schematically shown on the Figure.



Reversed Micellar Extraction

The aim of this study was to determine the partitioning of two kinds of enzymes ( $\alpha$ -amylase and  $\alpha$ -chymotrypsin) between aqueous phases and conjugate aqueous-in-oil microemulsions containing ionic surfactants. The cationic surfactant CTAB (cetyl trimethyl ammonium bromide) was used for the solubilization of ( $\alpha$ -amylase, whereas the anionic surfactant AOT (Aerosol-OT: sodium di-2-ethyl hexyl sulfosuccinate) was preferred for the removal of  $\alpha$ -chymotrypsin from the aqueous solution. The influence of the main factors affecting the enzyme solubilization, such as pH, surfactant concentration, and ionic strength were studied. The loaded reversed micellar solutions were stripped

using aqueous solutions with appropriate pH values and salt concentrations.

A simultaneous extraction and stripping of an enzyme was realized in a stirred transfer cell.

## 475.E1

### NONIONIC PERFLUOROPOLYETHER AMPHIPHILES

P. Lazzari<sup>1</sup>, A. Chittofrati<sup>1</sup>, S. Fontana<sup>1</sup>, P. Maccone<sup>1</sup>, C.M.C. Gambi<sup>2</sup>

<sup>1</sup>Ausimont-CRS, Bollate, Milano, Italy

<sup>2</sup>University of Florence, Arcetri, Firenze, Italy

A preliminary evaluation of the behaviour in aqueous solution will be presented for two nonionic surfactant mixtures obtained by reacting a perfluoropolyether (PFPE) precursor with long chain polyethoxylic amines, so to form two examples of amphiphilic materials of general structure

- a. PFPE - L -  $(\text{CH}_2\text{CH}_2\text{O})_n$  -  $\text{CH}_3$
- b. PFPE - L -  $(\text{CH}_2\text{CH}_2\text{O})_{2n}$  - L - PFPE

Evidence for micellization will be given in terms of surface tension, viscosity and light scattering measurements on dilute aqueous solutions, also supported by preliminary neutron scattering data. Basically, the two surface activity of the two mixtures was very similar, taking into account the slower diffusion rate of the larger specie *b*.

Such surfactants are particularly useful for the emulsification of PFPE oil-in-water, even at high concentration of dispersed phase: some examples of the very limited variation of droplet radius and polydispersity upon aging will be discussed on the basis of light scattering results.

## 476.E1 RHEOLOGY AND DRAG REDUCTION STUDIES ON CATIONIC SURFACTANT SOLUTIONS WITH MULTIPLE SUBSTITUTED BENZOATE COUNTERIONS

B. Lu<sup>1</sup>, Y. Zheng<sup>2</sup>, Z. Lin<sup>1</sup>, Y. Talmon<sup>3</sup> and J.L. Zakin<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, The Ohio State University, Columbus, OH 43210, USA.

<sup>2</sup>Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, USA.

<sup>3</sup>Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, 32000, Israel

Cationic surfactants with proper counterions have been shown to be effective as drag reducing additives and also to have unusual rheological behavior. They have strong viscoelastic characteristics and high extensional viscosity even at very dilute concentrations. The drag reduction effectiveness and rheological properties are greatly influenced by the nature of the counterions, however. In this paper, drag reduction and rheological properties are described for cetyltrimethylammonium chloride with benzoate counterions containing two or more of these substituent groups: chloro- methyl- nitro- and hydroxy-. Rheological results including first normal stress differences and extensional and shear viscosity measurements will be compared with drag reduction results. Micellar structures obtained by cryo-TEM techniques will also be compared. Differences in drag reduction, rheological properties and microstructures will be discussed in terms of differences in the chemical structures of the counterions.

## 477.E1 EFFECTS OF IONIC STRENGTH ON THE STABILITY OF DODECYLDIMETHYLAMINE OXIDE MICELLE AND THE HYDROGEN ION TITRATION PROPERTY

Hiroshi Maeda\*, Shuichi Muroi and Rie Kakehashi

Department of Chemistry, Faculty of Science, Kyushu University Fukuoka 812-81, Japan

Critical micelle concentrations (cmc) of dodecyldimethylamine oxide (DDAO) were determined at  $25 \pm 0.05^\circ\text{C}$  as a function of NaCl concentration  $C_s$  for both nonionic and cationic species by the surface tension measurements. The critical micelle concentration of the cationic species,  $\text{cmc}_+$ , was lower than that of the nonionic species  $\text{cmc}_0$  in the range of  $C_s$  higher than about 0.2 M, which strongly suggested an attractive interaction between the head groups of two cationic species in micelle, most probably the hydrogen bond. Logarithm of  $\text{cmc}_0$  decreased linearly with  $C_s$ , while logarithm of  $\text{cmc}_+$  gave a nonlinear dependence on logarithm of the counterion concentration  $C_g$ . The nonlinear Corrin - Harkins relation was discussed in terms of the salting-out contribution and/or micelle growth in addition to the electric free energy contribution. Surface excesses of both nonionic and cationic species were very similar and did not depend significantly on  $C_s$  up to 3 M NaCl. The surface tensions at surfactant concentrations above cmc,  $\gamma_{\text{cmc}}$ , decreased linearly either with  $C_s$  for the nonionic species or with  $\log C_s$  for the cationic species. Surface excesses of  $\text{Na}^+$  and  $\text{Cl}^-$  were evaluated by the Gibbs adsorption isotherm and compared with those expected from the double layer theory. The size of the nonionic micelles remained essentially constant over the entire range of  $C_s$  examined, while that of the cationics increased with  $C_s$  in the range  $C_s > 0.5$  M. At 1 M NaCl, growth of the micelle with the surfactant concentration was observed for the cationics but not for the

nonionics. Analysis of the titration data has revealed an extra work accompanying the ionization other than the electrostatic one. This can be attributed to the different stabilities of the hydrogen bonds between nonionic-cationic and cationic-cationic.

## 478.E1

### FAST INTERACTIONS IN MULTICOMPONENT SYSTEMS ON BASIS OF AQUEOUS SURFACTANT SOLUTIONS

V.G. Makarov, V.S. Sperkach, L.D. Kachanovskaya and F.D. Ovcharenko  
*Institute of Bio-Colloid Chemistry of National Academy of Sciences of Ukraine,  
Joint Laboratory of Medical Physics and Biocolloidal Systems, Kiev, Ukraine*

A range of acoustical, structural dynamical and physicochemical properties of multicomponent systems based on aqueous solutions of bis-quaternary ammonium ampholyte have been investigated by acoustic spectroscopy, viscometry and other methods in a wide range of concentration, temperature and ultrasound frequency. The systems studied comprised surfactant and components capable of forming associates or complexes, such as organic dyes and metal salts.

The data obtained have been used for calculations of a number of structural dynamical parameters of the solutions, such as classical sound attenuation, adiabatic compressibility, volume viscosity, relaxation strength, etc. It was established that the differences in the acoustical and structural dynamical properties display themselves most pronouncedly at temperatures below 313 K, while at higher temperatures they tend to level off, obviously as a result of intensification of molecular heat motion.

It was found that in the systems studied there are in total three separate relaxation processes going on in the frequency range from 5 to 3000 MHz. The fastest process (characteristic time  $1-3 \cdot 10^{-12}$  s) is related to weak interactions with participation of water molecules, the slowest one (characteristic time  $1-2 \cdot 10^{-8}$  s) belongs to large aggregate structures, while intermediate process was observed in the systems containing organic dye, which obviously plays an important role in structurization phenomena. In concentrated solutions all the processes observed are merging together in a continuous relaxation process with no separate regions distinguishable, testifying to the high degree of structural ordering in the system. Evidently, water in the systems studied exists both as a bulk phase of free solvent, and as water bound in hydration shells, while its state is being determined by interactions with large and less mobile structures formed by organic components and metal ions. Nature of the metal cation has relatively small influence on parameters of relaxation processes in the systems studied.

## 479.E1

### PARTITION COEFFICIENT OF ALKYLGLUCOSIDES BETWEEN WATER AND MICELLES DETERMINED BY THE DIFFERENTIAL CONDUCTIVITY METHOD

Masahiro Manabe, Miharū Kaneko, Hideo Kawamura  
*Niihama National College of Technology, Niihama, Japan*

When an amphiphasic substance is added in a micellar solution, it is partitioned between bulk water and micelles. The additive has the following two effects on the conductivity ( $\kappa$ ) of the micellar solution of an ionic surfactant. The one is the hydrophobic effect. The monomerically dissolved species in the bulk phase (concn.: Caf) enhances micellization of monomeric surfactant (concn.: Csf), which leads to the decrease in  $\kappa$ . The other is the electrostatic effect. The solubilized species (mole fraction in micelles: Xam) enhances the ionization degree ( $\alpha$ ) of micelles, due to the decrease in the surface charge density of micelles, which leads to decrease in  $\kappa$ . In the *differential conductivity method* for determining the partition coefficient ( $\kappa$ ) of alkanols, respective effects,  $k = dCsf/dCaf$  and  $d\alpha/dXam$ , were taken into account for the expression of  $\kappa$ .<sup>1,2</sup> The results for alkanols were as follows. (1)  $K$  increases with strength of hydrophobicity of alkanols. (2) The value of  $k$  is negative and in agreement with that of  $dCMC/dCa$  (the rate of CMC depression by the addition of alkanol). (3)  $d\alpha/dXam = 0.18$  was invariant for all alkanols (straight and branched chain) studied, which indicates that only the OH group contributes to the charge density effect. The conclusion suggests that the electrostatic effect becomes more remarkable as the head group size of the nonionic additive is larger. Then, in the present study,  $K$  of *alkylglucosides* in the SDS micellar solution has been determined by the

differential conductivity method. For octylglucoside, the higher value of  $d\alpha/dX_{am}=0.27$  than that for alkanols was obtained, where  $K=330$  is not so different from the value for 1-octanol. The ratio of the  $d\alpha/dX_{am}$  values is in good agreement with that of the size of these two hydrophylic groups. Therefore, it is concluded that the electrostatic effect depends on the head group size of the solubilize. The results together with other alkylglucosides will be discussed.

1. Manabe et. al., J. Colloid & Interface Sci., 115, 147 (1987).
2. Manabe et. al., The structure, Dynamics and Equilibrium Properties of Colloid Systems, 63-69, Kluwer Academic Publishers, Netherlands, 1990.

## 480.E1 THE CONFORMATION TRANSITIONS DURING ASSOCIATION OF THE DIPHILIC IONS IN AN AQUEOUS MEDIUM

Z.N. Markina, L.P. Panicheva, N.M. Zadymova

*Department of Chemistry, Moscow Lomonosov State University, Moscow, Russia*

With a view to establishing the connection between the aggregation and the conformation of diphilic ions in aqueous solutions, one has investigated precision electrical conductivity, the spectra of the light combination scattering (LCS) of sodium dodecyl sulfate (SDS) and chloride dodecyl dimethyl benzyl ammonium ( $C_{12}$  catamine), as well as the  $C_{12}$  catamine absorption ultraviolet spectra within a wide range of concentrations of surfactants solutions. In accordance with the electrical conductivity data within the region of high dilutions at various temperatures (283-333 K), one has estimated the form of monomers and SDS dimers. Using the LCS method, one has shown that the mobility of hydrocarbon chains in SDS dimers is greater than in monomers. The micelle formation within the region of critical micellar concentration ( $CMC_1$ ) is accompanied by an increase in the mobility, whereas the transformation of spherical micelles into spherocylindrical ones at  $CMC_2$  by a decrease in the mobility of hydrocarbon chains of diphilic ions.

## 481.E1 THE EFFECT OF TEMPERATURE ON THE CMC SHIFT IN THE WATER-SURFACTANT SYSTEMS WITH DIFFERENT ORGANIC ADDITIVES

Z.N. Markina, N.M. Zadymova

*Department of Chemistry, Moscow Lomonosov State University, Moscow, Russia*

Using a refractometric method comparative solubility of benzene, ethylbenzene, octane and cyclohexane in aqueous solutions of sodium soaps of saturated acids ( $C_6$ - $C_{14}$ ) below CMC at 293-333 K has been investigated. Precision conductometric and tensiometric measurements have shown, that by introducing of actually dissolved hydrocarbons into aqueous phase at various temperatures the promotion of micelle phase formation, that is decrease in CMC, takes place. The effect of hydrocarbons has been qualitatively explained by means of a statistic-thermodynamic model of hydrophobic bonding in water and aqueous solutions of hydrocarbons and surfactants. In contrast to hydrocarbons the introducing of organic additives decreasing the total polarity of aqueous phase (dioxane, methyl alcohol, ethylene glycol: up to 70 mol %) leads to increase in CMC. This increase is greater, the larger is the addition and the higher the temperature, this fact speaking for lowering of gain in energy by micelle formation in such systems as compared to pure solution of the surfactant. These investigations established that in solutions of sodium cholate and also in solutions of a soap with short chain - sodium caproate, if concentration of additives exceeds 5-12 mol %, micelles in mixed solvents are not formed (degeneration of micelles). As to solutions of long-chain soaps - sodium oleate and laurate - the tendency to form associates is kept up to 50-70 mol % of additives, though CMC can decrease in this case more than 50 times. The thermodynamic functions of micelle formation for investigated systems have been calculated. The method of CMC shift of surfactant in aqueous solutions under the effect of actually dissolved hydrophobic additions was used to show that the solubility in water of perfluorodecalin and perfluorotributyl amine at 293 K does not exceed  $2 \times 10^{-4}$  M. Using the precision tensiometric measurements for the aqueous solutions of perfluorononane acid at the interface with perfluorodecalin at 293 K as basis, one has evaluated an increment of the standard chemical potential for the

transition of  $\text{CF}_2$  - group from water to perfluoroorganic liquid and determined the solubility of perfluorodecalin and a number of perfluorocarbons ( $\text{C}_6$  -  $\text{C}_{12}$ ) in water.

## 482.E1

### SUGAR-BASED SURFACTANTS AS HYDROTROPES

Anna Matero and Åsa Petersen

*Institute of Surface Chemistry, Box 5607, 114 86 Stockholm, Sweden*

The term hydrotropy was introduced in 1916 by Neuberg to describe the increase in solubility of organic compounds in water by addition of certain compounds, so called hydrotropes. Traditional hydrotropes are characterised by a short and bulky structure, with a hydrophilic head group in combination with a short-chain hydrophobic group. The mechanism for hydrotropic action has been discussed in the literature and it has been found that hydrotropes destabilise ordered structure such as liquid crystalline phases. Hydrotropes are also used in cleaning formulation in order to facilitate the formulation. In this context they are used for elevating the cloud point of a solution containing nonionic surfactants. Sugar-based surfactants are a class of nonionic surfactants which are interesting as alternatives to ethoxylates, due to their ecological and technological properties. In this paper we report and present results for alkyl glucosides as hydrotropes. This study includes the determination of cloud point elevation for different nonionic surfactant solutions with additions of hydrotropes. The system pentanol/SDS/water has been used as a model system with isotropic regions as well as regions with liquid crystals in the phase diagram. The effect on these regions by adding sugar-based surfactants has been evaluated.

## 483.E1

### APPLICATION OF MOLECULAR FLUORESCENCE IN CHARACTERISTICS OF THE NONIONIC DETERGENTS AQUEOUS SOLUTIONS

Jacek S. Miller<sup>1</sup>, Marian Wolszczak<sup>2</sup>

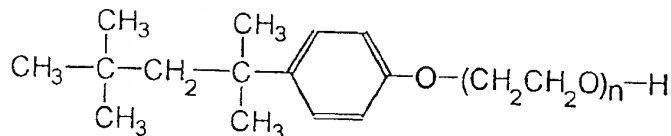
<sup>1</sup>*Technical University of Łódź, Faculty of Process and Environmental Engineering*

<sup>2</sup>*Institute of Applied Radiation Chemistry, Łódź, Poland*

For years micellar solutions and microemulsions have been the object of extensive study in order to understand their physicochemical properties. Works are now in progress to use these solutions as new media in a number of applications. The knowledge of the dependence of the micelle molecular weight or aggregation number ( $N$ ) on the surfactant concentration is both practical and theoretical interest.

Fluorescence probe analysis is becoming an important area in studies of multimolecular aggregates such as micelle and membranes. Fluorescence techniques (steady-state, quenching, time resolved) have been used with great success in the study of surfactants micelle. They are useful not only for critical micelle concentration (CMC) determination but also for measuring the  $N$  of the micelles.

The investigated detergents belong to a very popular family of nonionics, obtained via condensation of  $p$ -(1,1,3,3-tetramethyl)phenol with ethylene oxide. They are known under trade name Triton®<sup>1</sup>. These surfactants are not easily biodegradable however they are widely applied in the industry and house keeping. Tritons are also the subject of considerable attention in both academic and industrial circles. The general formula is as follows:



The number of ethoxyl groups  $n$  in commercially available ethoxylated phenols change from 1 to 60. Each product is a mixture of homologues which differ in the hydrophilic chain length.

The aim of the work was to compare different fluorescence techniques of the CMC and  $N$  determination and to correlate the obtained values with the average number of the oxyethylene groups in the hydrophilic chain.

The objects of studies were seven various Tritons listed below:

Surfactant	From	n	M <sub>w</sub>
Triton X- 15	Sigma	1	250
Triton X-35	Sigma	3	338
Triton X-45	Fluka	5	426
Triton X- 114	Fluka	8	558
Triton X- 100	Fluka	9.5	624
Triton X-305	Merck	30	1526
Triton X-405	Fluka	40	1966

In this work we used pyrene as the fluorescent probe, which is suitable for such purposes - notably the long life-time of its monomers and efficient formation of excimer. In the presence of detergents, pyrene in water (below  $10^{-6}$  M) undergoes several spectroscopic changes. Among them there is a red shift of the band in the excitation spectrum from 334 nm to 338.5 nm, an increase in the intensities of first peak relative to third peak in the vibrational fine structure of the pyrene fluorescence, an

appearance of broad band (~480 nm), attributed to pyrene excimer fluorescence. These changes were used to determine CMC.

An attempt to determine N were carried out using two methods. First, based on quenching of the pyrene luminescence in micellar solution. Second, which involves excimer formation by micelle solubilized pyrene and lie in measurement of the fluorescence decay curves.

<sup>1</sup>Triton is trade mark of the Rohm und Hass Deutschland GmbH

## 484.E1

### SOLID AND SOLUTION PROPERTIES OF ALKYLAMMONIUM PERFLUOROCARBOXYLATES\*

Yoshikiyo Moroi, Hiromi Furuya, and Kozue Kaibara

*Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812-81, Japan*

Seven alkylammonium perfluorocarboxylates ( $C_nH_{2n+1}NH_3^+C_mF_{2m+1}COO^-$ ;  $n+m = 15$ ,  $n = 2, 4, 6, 8, 10, 12, 14$ ) were synthesized, and their physico-chemical properties were investigated. Melting points (mp) and heats of fusion of the solids were determined by the differential scanning calorimetry, and the crystal structures were examined by the X-ray diffraction analysis. The critical micelle concentration (CMC) and aqueous solubility for  $C_{14}H_{29}NH_3^+CF_3COO^-$  and  $C_{12}H_{25}NH_3^+C_3F_7COO^-$  were obtained from the electric conductivity method, while the reproducible data were not obtainable for the other five amphiphiles. The size of the molecular aggregates was observed by the phase contrast microscope, and very large aggregates of micrometers in size were found to be formed. These results indicate that the properties of solids and solutions depend not only on hydrocarbon but also on fluorocarbon chains. The time-dependence of the electric conductance was traced immediately after dilution of concentrated  $C_4H_9NH_3^+C_{11}F_{23}COO^-$  solution, and the dissociation rate of the aggregates to monomers was obtained over the temperature range from 20 to 45°C. The activation energy of the dissociation process was found to be 76 kJ mol<sup>-1</sup>.

\*The Journal of Physical Chemistry, 100 (43), 17249-17254 (1996).

## 485.E1

### INFLUENCE OF SOME ADDITIVES ON THE PHASE BEHAVIOUR OF THE SYSTEM TRYTON X-114 - WATER

S. Panayotova<sup>1</sup>, R. Marinov<sup>2</sup> and A. Derzhanski<sup>2</sup>

<sup>1</sup>*Department of Physics, High Institute of Food and Flavor Industries, 4000 Plovdiv, Bulgaria*

<sup>2</sup>*Institute of Solid State Physics, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria*

The phase behavior of the system Tryton X-114 - water in the presence of an octanol, butanol, fructose and glucose have been investigated. The experimental data are compared with the results of recently proposed model<sup>1</sup> of the phase transitions in lyotropic liquid crystal systems.

The main result is that the influence of the octanol is more pronounced in comparison with the sugars. The experimental data show that the octanol displaces the lamellar phase to higher Tryton's concentrations probably because it has the tendency to be solubilized in the core of the micelles where its longer hydrophobic chain is better situated. On the other hand, the sugars must be easily solubilized in the oxyethylene region of the micelles and should destabilise the lamellar phase.

We described the phase behavior of the above mentioned systems by means of our model<sup>1</sup>. We considered an elementary molecular complex (EMC) which consists of one Tryton's molecule and a molecule of the additive (octanol or sugar). The additives are solubilized in the different places along the Tryton's molecule which leads to changes of the EMC's shape. According to our model such shape changes will lead to experimentally observed displacement of the lamellar phase to higher Tryton's concentration.

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## **486.E1 THE INFLUENCE OF MOLECULAR SIZE OF NONIONIC SURFACTANTS ON DYNAMIC SURFACE TENSION, BUBBLE SIZE AND FOAM STABILITY**

**Rhitu Rao and Per Stenius**

*Laboratory of Forest Products Chemistry, Helsinki University of Technology Espoo, Finland*

The kinetics of formation of adsorbed surfactant layers and its relationship to formation of bubbles, bubble characteristics and foam stability has been investigated for a number of surfactants of the type used as flotation agents in flotation deinking. In particular, the aim has been to understand the importance of molecular size in parallel to the hydrophobic/hydrophilic balance of the surfactants.

The dynamic surface tension of aqueous solutions of a range of alcohol ethoxylates were determined using maximum bubble pressure method. Their influence on the maximum bubble size, number of bubbles and bubble size distribution of bubbles was determined using an image analysis system. The bubbles were formed by passing gas into the solution through a porous plate. The stability of foams formed by the same solutions was studied using Bikerman type apparatus.

The dynamic surface tension data are interpreted in terms of current theories of rate of formation of surfactant layers and surface coverage with emphasis on effects of molecular size. The relationship of these results to bubble characteristics and foam properties is discussed.

## **487.E1 HYDROPHOBIC INTERACTION OF ZWITTERIONIC HEMICYANINE DYES WITH MICELLES OF THE ANIONIC AND CATIONIC SURFACTANTS**

**S.S. Shah, M.A. Awan, Hadayat Ullah, K. Naeem, G.M. Laghari**

*Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan*

An aqueous micellar solution has the ability to solubilize a wide variety of organic additives with quite distinct polarities and degree of hydrophobicities. Partitioning of the solute between aqueous bulk medium and the micelles may serve a model to predict solubility of dyes/drug molecules in biological membranes, globular proteins. The amphiphilic hemicyanine dyes, are used as effective voltage sensitive probes in biomembranes, neurons, culture and brain<sup>1</sup>.

The solubilization of zwitterionic dialkylammino (dimethyl to dihexyl) stilbazoliumbutyl sulfonate dyes into the micelles of anionic and cationic surfactants has been studied. It is known that the cmc lowering ability can be linked to the partition coefficient of the organic additive between the micelles and the aqueous bulk phase<sup>2</sup>. The micelle-water partition coefficient ( $K_x$ ) and standard free energy change of solubilization ( $\Delta G_p^0$ ) of these dyes in CTAB micelles were determined by conductance and differential absorbance measurements<sup>3</sup>. With increasing surfactant concentration an increase in the differential absorbance ( $\Delta A$ ) and spectral red shift reflects the stronger interaction and enhanced solubility of the dyes.

The anionic surfactants like SDS and SDBS exhibited even stronger interaction with the hemicyanine dyes. The hydrophobic interaction of the dyes with varying hydrophobicities in various surfactant solutions has been discussed. Different quantities like peak shift,  $K_x$ ,  $\Delta A$ ,  $\Delta G_p^0$ , number of dye molecules per micelle ( $n$ ) and interaction parameter ( $\theta$ ) for these dyes in different surfactant solutions were determined.

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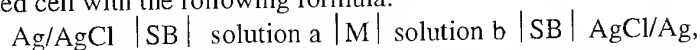
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## 488.E1 THERMODYNAMICS OF TRANSFER FOR ALKYL PYRIDINIUM HALIDES FROM WATER TO ALKANOL-WATER MIXED SOLVENTS

K. Shirahama, Y. Kawahara, T. Nishida, and N. Takisawa  
*Department of Chemistry, Saga University, Saga 840, Japan*

Free energies of transfer for alkylpyridinium halides ( $C_{12}$ ,  $C_{14}$ ) from water to alkanol( $C_1$ - $C_4$ )-water mixed solvents are determined by a surfactant-selective electrode. The sensor membrane is composed of partially sulfonated PVC and polymerized plasticizer so that there is no worry about dissolution of the membrane components into the mixed solvents assuring a long life time of electrode performance. The electrode is essentially a concentrated cell with the following formula:



where SB is an agar salt bridge(KCl), M the sensor membrane. The electromotive force of the cell shows an asymmetric potential when, for a surfactant, different solvents are placed in solutions a and b. The asymmetric potential is related with free energy of transfer. The free energy of transfer thus obtained decreases with addition of alkanol. It is understood that the surfactants "like" alcoholic atmosphere. This tendency is getting more marked with increase in chain length of alkanol. From temperature dependence of free energy of transfer, enthalpy and entropy of the corresponding process are calculated. The enthalpy of transfer increases first and then decreases passing through a maximum. The maximum shifts to lower alkanol concentration for a longer alkanol chain length. The positive enthalpy change is thought to be caused by melting down hydrophobic hydration around surfactant alkylchain on encountering alkanol molecules. This is seen in the entropy of transfer which is always positive and has correspondingly a maximum: one of the manifestation of release of water molecules from the hydration shell resulting in an entropy increase. The alkanol concentrations where the enthalpic and entropic maxima appear exactly coincide with those of extremes of partial molar volumes of water and alkanol in the binary systems. The enthalpy and entropy of transfer delicately compensate with each other giving a smooth decrease in the free energy of transfer.

## 489.E1 MIXED BINARY SYSTEMS WITH ALKYLGLYCOSIDES: EFFECT OF THE POLAR HEADGROUP

M.L. Sierra\*, M. Svensson  
*Institute for Surface Chemistry, Box 5607, S-114 86 Stockholm, Sweden*

Mixtures of the anionic surfactant, SDS, and different alkylglycosides ( $C_nG_m$   $m=1$   $n=8-12$ ,  $m=2$   $n=10-14$ ) have been studied in order to find out whether there exists synergism or not in the micelle formation. The influence of the alkyl chain length and the number of glucose units in the headgroup on the behaviour of the mixed systems has been investigated. Surface tension measurements were carried out and the results were analysed in terms of Rubingh's theory. Synergism in the mixed micelle formation was obtained for the systems formed with  $C_8G_1$ ,  $C_{10}G_1$  and  $C_{10}G_2$ , but none of the systems presented synergism when surface tension reduction efficiency and effectiveness were considered. In fact, the results show a non-constant trend of the interaction parameter values,  $\beta$ , along the nonionic surfactant molar ratio. This behaviour is more apparent in the  $b$  values obtained for the interaction in the mixed monolayer,  $\beta^\sigma$  (efficiency in the surface tension reduction), than in the mixed micelle formation,  $\beta^M$ . In the former there exists a linear decrease of the  $\beta^\sigma$  from very small molar ratios while in the mixed micelle formation they remain almost constant up to a molar ratio value of around 0.6, from which it also decreases.

Furthermore, mixed systems of the nonionic, surfactant  $\beta$ -decylglucoside ( $C_{10}G_1$ ) with the zwitterionic dodecylsarcosine at different pH (pH=3, 7 and 10) were studied as well as with a nonionic ( $C_{12}E_5$ ) and a cationic ( $C_{12}TAB$ ) surfactants. The alkyl chain length was kept constant ( $C_{12}$ ) and close to the chain length of the nonionic  $\beta$ -decylglucoside since our aim was to study the effect of different polar head groups in the mixed systems following the trend nonionic-anionic, nonionic-nonionic, nonionic-cationic and nonionic-zwitterionic, under the best conditions of interaction between the surfactants, i.e. when the alkyl chains have almost the same length. The results obtained for the different systems are shown in the present work.



## 490.E1

## STEROL-BASED SURFACTANTS

Martin Svensson, Britta Folmer and Krister Holmberg  
*Institute for Surface Chemistry (YKI), Stockholm, Sweden*

It is a well known fact that cholesterol in the body has the effect of stabilising the lipid bilayer in membranes. Similarly, it is also known that cholesterol has the ability to stabilise lipid layers *in vitro*, e.g. in liposomes.

We have investigated the physical chemical behaviour of several surfactants based on cholesterol and phytosterol. The structure of the hydrophilic moiety has been varied in a systematic way and the effect on the amphiphilic properties has been investigated (e.g. phase behaviour, surface adsorption). The behaviour is compared to previous reports in the literature and potential applications will be discussed.

The results give information on how the hydrophobic sterol-based part of the surfactant affects the physical properties. This is of importance when commercial preparations of alicyclic compounds (e.g. cholesterol, sitosterol, abietic acid) are used as raw material in surfactant production. The results are relevant for formulations where such surfactants are one of several components. This will be of relevance in the production of new industrial surfactants based on natural products.

## 491.E1

DYNAMIC INTERFACIAL TENSION OF TRISILOXANE AND  
HYDROCARBON NONIONIC SURFACTANTS AND THEIR SPREADING BEHAVIOR ON  
HYDROPHOBIC SURFACE S

T.F. Svitova<sup>1</sup>, C.J. Radke<sup>2</sup>, Randal M. Hill<sup>3</sup>

<sup>1</sup>*Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia*

<sup>2</sup>*University of California at Berkeley, Berkeley, USA*

<sup>3</sup>*Dow Corning Corp., Midland, Michigan, USA*

In many cases, for instance, during wetting and spreading, emulsification, foaming and dispersion formation, the processes in the presence of the surfactants take place under non-equilibrium conditions and in these cases the dynamic properties of the surfactant adsorption layer are of great importance. One of the methods to investigate amphiphile adsorption kinetics at freshly formed interfaces is to measure the dynamic interfacial tension. Dynamics of surface (at the solution/air interface) and interfacial (at the solution/n-dodecane and solution/n-hexadecane interface) tension of nonionic siloxane surfactants, some of which are known as "super-wetter", and ethoxylated dodecyl- and iso-dodecyl alcohols were studied by Growing Drop, Drop Volume, Drop Weight and Pendant Drop methods. The influence of surfactant concentration and hydrophilicity (length of ethoxy-chain) on surface/interfacial tension dynamics and spreading of aqueous solutions on the liquid hydrocarbons surface was investigated. Surface and interfacial tension fall rates were estimated on the base of Hua and Rosen approach. It was found that concentrated solutions of siloxane surfactants with moderate ethoxy-chain length show unusually high surface/interfacial tension fall rate. These solutions spread very fast over a liquid hydrocarbon surface: a drop of aqueous solution with a volume about 3  $\mu\text{l}$  forms a thin spreading film with an area of several  $\text{cm}^2$  in 5-10 s. Rate of spreading and resulting film thickness were found to depend on surfactant concentration and hydrophilicity and hydrocarbon sub-phase chain length. A good correlation between surface/interfacial tension fall rate, rate of spreading and dynamic spreading coefficient was found. Diffusivity of these surfactants were evaluated according to (Fainerman V., Makievski A., Miller R. *Colloids and Surfaces*, A, 1994, 87, 61) and it was found that for the siloxane surfactant with 8 ethoxy-groups the diffusion coefficient values are one order of magnitude higher than that of the hydrocarbon analogue with 5 ethoxy-groups in all surfactant concentration range studied. An increase of ethoxy-chain length as for siloxane so as for hydrocarbon surfactants causes a decrease of diffusion coefficient and surface/interfacial tension fall rate and leads to suppressing of surfactant spreading ability.

## 492.E1 THERMODYNAMICS OF THE TEMPERATURE AND PRESSURE EFFECTS ON THE SOLUBILITY OF SURFACTANTS IN WATER

Mitsuru Tanaka, Yoshio Murata  
Fukuoka University, Fukuoka, Japan

The solubility of surfactant in water rapidly increases with the increase of temperature above the Krafft temperature. On the other hand, the pressure of the micellar (m) solution coexisting with surfactant solids (c) being raised, the total concentration rapidly decreases up to a certain pressure  $P_c$ , above which the concentration only gradually decreases. This has been explained by the absence of micelles at pressure higher than  $P_c$ .

Applying small system thermodynamics to the equilibrium between the micellar solution and surfactant solids, we obtained the equations which well explain the temperature and pressure effects not only on the solubility but also on the monomer and micelle concentrations,  $C_i$  and  $C_m$ , and micellar aggregation numbers,  $\bar{N}_i$  and  $\bar{N}_i^2$  in multicomponent surfactant system. For single component surfactant systems, for example, we obtained:

$$\begin{aligned} (\partial C_i' / \partial T)_P &= [C_i(\bar{S}_i^s - S_i^c) + C_m \bar{N}_i^2 (\bar{S}_i^m - S_i^c)] / kT \\ (\partial C_i' / \partial P)_T &= -[C_i(\bar{V}_i^s - V_i^c) + C_m \bar{N}_i^2 (\bar{V}_i^m - V_i^c)] / kT \end{aligned}$$

where  $\bar{S}_i^s$ ,  $\bar{S}_i^m$  and  $S_i^c$  are respectively the partial molar entropies of the monomeric species in solution, micelles and solid. Since  $\bar{S}_i^m > S_i^c$  and  $\bar{V}_i^m > V_i^c$ , the equations show that as far as  $C_m$  has definite values, solubility  $C_i'$  rapidly increases with temperature, while rapidly decreases with pressure.

## 493.E1 A KINETIC STUDY OF THE REACTION BETWEEN SOLUBLE (COLLOIDAL) MANGANESE DIOXIDE AND FORMIC ACID IN AQUEOUS PERCHLORIC ACID SOLUTION IN THE PRESENCE OF SURFACE ACTIVE AGENTS

M. Tunçay, N. Yüce, B. Arikan, S. Göktürk  
University of Istanbul, Department of Chemistry, Avcılar, 34850 Istanbul Turkey

The kinetics of the reaction between a soluble form of colloidal manganese dioxide (obtained by reduction of potassium permanganate with sodium thiosulfate) and formic acid at 25 °C and constant ionic strength in aqueous perchloric acid solution were studied in the presence of surface active agents, cationic (Cetyltrimethylammoniumbromide-CTAB), anionic (Sodium Lauryl Sulfate - NaLS), nonionic (Triton X-100).

The reaction rate was followed spectrophotometrically by measuring the changes in absorbances at 500 nm. The results were analysed by means of fixed time method.

Cationic surfactants caused flocculation of the oppositely charged colloidal  $MnO_2$  and could not be used. Whereas anionic micellar systems were found to be ineffective in reaction rate. No noticeable effect of NaLS on the reaction rate was observed even at the high concentrations.

This reaction was found to be accelerated by nonionic micelles of Triton X-100. The first-order rate constant,  $k$  increased as Triton X-100 concentration increased and reached a plateau at the higher concentrations.

## 494.E1 CHANGES IN FORM AND RELATIVE STABILITY OF MICELLES IN MULTICOMPONENT SYSTEMS

N.Vila Romeu<sup>1</sup> and G. Taddei<sup>2</sup>

<sup>1</sup>*Departamento de Fisico-Química, Facultad de Farmacia, Universidad de Santiago de Compostela, Spain*

<sup>2</sup>*Dipartimento di Chimica dell 'Università', via G. Capponi 9, Florence, 50121 Italy*

Calculations of the relative stability of different micelle forms in surfactant multicomponent (more than two) systems were performed on the basis of the surfactant parameter model. The results show that some particular micelle forms which are of little relative stability in a binary water-surfactant system, are strongly stabilized by the presence of cosurfactants whose molecules fit well in micelle zones of distinct curvatures.

## 495.E1 EQUILIBRIUM ADSORPTION OF TRITON X-100 FROM AQUEOUS SOLUTIONS ON POROUS AND NONPOROUS CARBON SURFACE

N.A. Yaroshenko

*Institute of Sorption and Endoecology of the National Academy of Science of Ukraine,  
30/32 Shelkovichnaya st., Kiev 252024, Ukraine*

A structure of the adsorption layer of micelle-generating surfactants on the surface of nonporous nonpolar sorbent has not been determined. There is a contradictory information about this question in literature. The most of the studies on surfactant adsorption from solutions on surfaces of solid bodies were performed by the conventional method of constant sorbent load. In this study, the conventional method and the method of constant degree of surfactant removal  $C_r$  of solution have been used.

The adsorption isotherms of triton X-100 on graphitized black with different degree of surfactant removal from solutions (10, 20, 30, 40, 50) were obtained. The most of adsorption isotherms are double-stage ones. On the first stage of adsorption saturation, a monomolecular adsorptive layer with various variants of polyoxiethylene group orientation is formed: beginning of horizontal orientation at  $C_r = 10\%$  to vertical one at  $C_r = 50\%$ . Alkylphenyl radical of this molecule has oriented by the longitudinal axis exceptionally in parallel to the carbon surface. On the second stage of absorption saturation, the three-dimension associates are formed.

At the same quantities of  $C_r$ , the adsorption isotherms of triton X-100 on activated carbon AG-3 were obtained. Depending on the content of solid phase in a system, the isotherm form changes from the Langmuir type to the isotherm with a clearly pronounced maximum.

The values of Gibbs adsorption energy for triton X-100 on graphitized black and activated carbon are close and are not dependent on the concentration of a solid phase in the system.

The studies of equilibrium adsorption of the systems mentioned by the method of constant degree of surfactant removal of solution provided to solve some contradictions on this question.

## 496.E2 KINETICS OF IONIC SURFACIANT ADSORPTION AT LIQUID/LIQUID AND FREE INTERFACES

Z. Adameczyk, G. Para and P. Warszynski

*Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, ul. Niezapominajek 1,  
30-239 Krakow, Poland*

A theoretical approach was developed for analysing nonstationary adsorption from multicomponent surfactant solutions at spherically shaped fluid/fluid interfaces. The boundary conditions in the bulk and at the interfaces, both in the kinetic form and in terms of nonlinear adsorption isotherms, were discussed. In the case of ionic surfactant the governing Poisson-Boltzmann equation was added to the calculation scheme enabling one at a quantitative determination of the double-layer effect on adsorption kinetics. To solve the bulk and surface mass balance equations a general numerical method was formulated based on the extension

of the implicit finite difference Crank-Nicholson scheme. The validity of the theoretical approach was illustrated by comparison with experimental data concerning adsorption of both nonionic (dioxanes) and ionic (CTAB, SDS) surfactants and their mixtures at mercury/electrolyte and electrolyte/air (free) interfaces. In the former case the precise tensammetric method was applied and in the latter the surface tension measurements (drop weight method) were used for determining adsorption kinetics and adsorption isotherms. It was found that the experimental kinetic data collected for various bulk surfactant concentrations were in a quantitative agreement with the theoretical predictions. Also the effect of the ionic strength and electrolyte composition correlated well with our theoretical model. It was also found that the adsorption isotherms can adequately be reflected by either the Langmuir or Frumkin adsorption model whereas the nonlocalized adsorption model stemming from the scaled particle theory proved less accurate. It was concluded that this behaviour can be attributed to the attractive lateral interactions among adsorbed molecules. The experimentally determined  $\Delta G^0$  values indicated that adsorption of all surfactants was considerably stronger and consequently less selective for the mercury/electrolyte interface.

## 497.E2 APPLICATION OF LINEAR SOLVATION ENERGY RELATIONSHIPS FOR ADSORPTION OF METAL EXTRACTANTS AND MODIFIERS AT ORGANIC SOLVENT/WATER INTERFACES

W. Apostoluk<sup>1</sup> and J. Szymanowski<sup>2</sup>

<sup>1</sup>*Institute of Inorganic Chemistry and Metallurgy of Rare Elements,  
Technical University of Wrocław, Wrocław, Poland*

<sup>2</sup>*Institute of Chemical Technology and Engineering, Poznań University of Technology, Poznań, Poland*

Metal extractants can be considered as hydrophobic surfactants well soluble in hydrocarbon solvents. Extraction of metals with such extractants occurs according to the interfacial mechanism with preadsorption of extractant and modifier molecules at hydrocarbon water interfaces. As a result, the adsorption behavior and distribution of extractant and modifier between both phases become important parameters which affect the rate of extraction. Interfacial concentration, molecule orientation and the free energy of adsorption are the most important parameters. Linear solvation energy relationships, based on application of Kamlet and Taft model were modified and the following model was used  $X = \phi(\pi^*, \alpha, \beta, \delta_H^2, c, \text{HLB})$  where X stands for a correlated adsorption parameter or distribution coefficient,  $\pi^*$  describes the dipolarity polarizability effects,  $\alpha$  and  $\beta$  are the parameters of solvent ability of hydrogen bond donation and acceptance, respectively,  $\delta_H^2$  is the solvent cohesive energy density, c stands for the concentration in the hydrocarbon phase and HLB is the hydrophile lipophile balance. Statistically valid semiempirical relations were obtained for hydrophobic hydroxyoximes (copper extractants) and alcohols in extraction systems containing various hydrocarbons (aliphatic, cyclic, aromatic and chlorinated hydrocarbons) as the organic phase. The linear solvation energy relationships contain separated effects of extractant or modifier concentration, solute hydrophobicity and solvent properties. These equations can be used to predict and verify the values of the considered parameters in systems containing various solvents and their mixtures.

## 498.E2 ADSORPTION OF HYDROPHOBIC PYRIDINECARBOXAMIDES AT TOLUENE/WATER INTERFACE

J. Blaszczyk, M.B. Bogacki, A. Borowiak-Resterna and J. Szymanowski

*Institute of Chemical Technology and Engineering, Poznań University of Technology, Poznań, Poland*

Metal extractants can be considered as hydrophobic surfactants well soluble in hydrocarbon solvents. Hydrophobic pyridinecarboxamides are proposed as extractants for copper recovery from chloride solutions. The reaction between neutral copper chlorocomplex  $\text{CuCl}_2$  and extractant molecule occurs in the aqueous film at the interface. The adsorption behavior of extractant molecules, i.e. the interfacial concentration, orientation and Gibbs free energy of adsorption are important parameters which affect the rate of extraction in kinetic regime. The interfacial tension isotherms were determined by the drop volume method for various pyridine carboxamides having one or two amide groups  $\text{CONHR}$  or  $\text{CONR}_2$  located at various positions of the pyridine ring. The Szyszkowski adsorption parameters, the surface excess, molecular area and the Gibbs

free energy of adsorption were calculated. A great effect of extractant structure on adsorption at the toluene/water interface was observed. The effect of the amide group type (CONHR or CONR<sub>2</sub>) is stronger than the effect of the alkyl group length. The effect of the substituent position in the pyridine ring (3 or 4) is relatively weak. However, a significantly higher interfacial activity is observed for extractants having the amide group CONHR at position 2. The observed effects can be well explained by the molecular modeling used to determine the structures of the extractant molecules and their hydrates and their probable orientations at the interface. The oxygen atom of the amide group(s) is first hydrated. Pyridine nitrogen is hydrated, too, but the hydration of the amide nitrogen is not observed. The type of the amide group affects the molecule orientation at the interface. High interfacial activity of extractants having the amide substituent at position 2 in the pyridine ring can be explained by formation of hydrates with cyclic structures, as predicted by the molecular modeling.

## 499.E2

### THERMODYNAMIC STABILITY OF DISPERSE SYSTEMS. HETEROGENEOUS ISOTHERMAL OPEN SYSTEM

G. Bliznakov and Sv.P. Delineshev

*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The effect of impurities on the thermodynamic stability in an open heterogeneous system has been investigated. The impurities are surfactants, i.e. after their adsorption on the interface, they cause a change ( $\Delta\sigma$ ) in specific surface energy of the dispersed phase. According to the sign and value of  $\Delta\sigma$ , the impurities have been given the names of "inactive surfactant", "negative surfactant" and "positive surfactant".

A heterogeneous system with an impurity present in an amount not sufficing to form a monolayer coverage on the surface of the dispersed phase has been studied.

The case when the impurity present is enough to form a monolayer coverage on the surface of the dispersed phase in the open heterogeneous disperse system has been investigated in [1].

Attention has been paid to the fact that the presence of a surfactant with an activity within the range  $0 < \Delta\sigma < \sigma_0$  ( $\sigma_0$  is the specific surface energy of an adsorption-free surface of the dispersed phase) reduces the thermodynamic force for the appearance of the Gibbs-Thomson effect and for the recrystallization (recrystallization) processes in the heterogeneous polydisperse system.

It has been shown that when the impurity possesses the activity  $\Delta\sigma = \sigma_0$ , the supersaturation becomes zero and the condensed phases should be (irrespective of their sizes and shapes) in equilibrium with one another because their vapour pressure becomes equal to that of infinitely large phase. In this case the Gibbs-Thomson effect completely disappears, the system becomes thermodynamically stable and, regardless of its polydispersity, it can exist infinitely long. The behaviour of such a heterogeneous system, which is far from its critical point (the system temperature is  $T \ll T_{\text{critical}}$ ), is similar to the behaviour of a system in the region of its critical point: the surface tension becomes nearly equal to zero, and the fluctuations sharply increase.

The case when the surfactant activity is so high ( $\Delta\sigma > \sigma_0$ ) that  $\sigma_a = \sigma_0 - \Delta\sigma < 0$  ( $\sigma_a$  is the specific surface energy of the interface in the presence of an adsorbed surfactant), is of a special interest. It represents a paradox in the phase formation theory: as a result of the adsorption of an impurity with such a high activity, the surface of the condensed phase would be destabilized and the phase would be spontaneously dispersed.

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## 500.E2

### INTERFACIAL ACTIVITY IN ALKALI/ACID OIL SYSTEMS AND THE REDUCTION OF THE INTERFACIAL TENSION

Pablo Contreras\*, Mihaela Olteanu

*University of Bucharest, Physical Chemistry Department, Laboratory of Colloids, Bucharest, Romania*

*\*Ph.D. Student of INTEVEL, S.A. Venezuela.*

The interfacial activity of some carboxylic acids and its salts, formatted *in situ*, has been studied in alkali/acid oil systems. The study was conducted in order to obtain an approximation of the physicochemical

mechanisms responsible for lowering of interfacial tension in these systems. Oleic and Cyclopentane carboxylic were the acid compounds used, n-decane the oil phase and sodium hydroxide solution the alkali. The ionic strength was kept constant with the addition of sodium chloride.

The synergetic effect of the acid-salt adsorbed and the possibilities of a complex formation were analyzed according with the theory of abnormal hydrolysis of Lucassen. The role of the adsorbed acid as cosurfactant was explained too. The surface pressure relationship taking the kinetic and electrical contributions of adsorbed species to estimate the interfacial tension has been modified. The second term of the Frumkin isotherm was considered.

A system chemistry for the contacting of an acidic oil with the alkali solution was suggested. The experimental values of interfacial tension were obtained studying the geometry of the meniscus formed by the two phases in a rotating capillar. The technique has permitted to fix the volumetric phase relation 1:1 and thus avoid changes which are expected to affect the relative rates of desorption of the surfactant from the interface. An approximation of the differential equation solution describing the shape of the meniscus was reached with a computing program. The approach developed by Bashforth and Adams and extended by Sugden was used to obtain the ratio of curvature at the apex. The values of interfacial tension match with the values calculated from the surface pressure relationship.

## 501.E2

### SURFACE PRESSURE OF PROTEIN ADSORPTION LAYERS: APPLICATION TO MOLECULAR MASS MEASUREMENT

R. Douillard

*Biochimie des Macromolécules Végétales, UPBP, INRA, CRA, 2 Esplanade R. Garros,  
BP 224, 51686 Reims cedex 2, France*

The equation of state of proteins adsorbed at the air/buffer interface has been approximated by the ideal as law in the gaseous regime (Guastalla, 1939) or by laws assuming that proteins are non-penetrable objects defined by a constant surface area (constant surface area model) when deviation from the ideal case is too large (Bull, 1950; Lucassen-Reynders, 1994). These models give a good fit to the experimental data only at moderately low surface concentrations. Since a few years, the adsorption layers of proteins have been modelised, in a scaling law approach, as multiblock copolymer layers (Douillard, 1994; Aguié-Béghin et al., 1997). The fit to the experimental data is good when the previous models do not hold any more. The ideal as law is a limiting, case of the constant surface area model but the scaling law description cannot reduce to the other models when the surface concentration is lowered. In this communication, a model is proposed where the adsorbed molecules behave either as constant area solids at relatively low concentrations or as multiblock copolymers at higher values.

Molecular mass of proteins have been calculated from the isotherms assuming an ideal gas law or a constant surface area behaviour (Guastalla, 1939; Bull, 1950; Demeny et al., 1966; Ohnishi et al., 1994). However, when the experimental data belong to the multiblock copolymer regime, they cannot fit the previous model and the molecular mass measurement may be erroneous. An evaluation of that systematic error is made, as a function of the relevant parameters.

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**502.E2****NEW INSIGHT INTO THE ADSORPTION MECHANISM OF  
CARBOXYLIC ACID AT THE SURFACE OF TITANIUM DIOXIDE****Jaroslav Drelich***Department of Metallurgical Engineering, University of Utah, WBB 124, Salt Lake City, Utah 84112, USA*

The adsorption of oleic acid at the surface of titanium dioxide from aqueous solutions was examined by Fourier transform infrared (FT-IR) spectroscopy using a germanium internal reflection element coated with a thin film of  $\text{TiO}_2$ . This thin film with a thickness of 100-200 Å, was deposited on the surface of a germanium single crystal by RF magnetron reactive sputtering. It was found that significant adsorption of oleic acid/oleate from a 0.02-0.03 mM aqueous solution on the surface of  $\text{TiO}_2$  thin film occurs at neutral pH, from about pH=5.5 to pH=7.7. Adsorption of oleic acid/oleate at the surface of the amorphous  $\text{TiO}_2$  thin film appeared to be physical and reversible. The adsorption isotherm obtained in this study relates well with the distribution of an acid-soap dimer  $(\text{RCOO})_2\text{H}$ . This experimental result supports prediction made by some of the researchers that the acid-soap dimer is an important component of carboxylic acid solution actively involved in the formation of an adsorbed carboxylate layer at the surface of titanium dioxide.

**503.E2****EFFECT OF SUBSTRATE HYDROPHOBICITY  
ON SURFACE-AGGREGATE GEOMETRY: ZWITTERIONIC AND NON-IONIC SURFACTANTS****William A. Ducker and Lachlan M. Grant***Department of Chemistry, University of Otago, P. O. Box 56, Dunedin, New Zealand*

Atomic Force Microscopy (AFM) has been used to determine that the zwitterionic surfactant, dodecyltrimethylammonio propane sulfonate (DDAPS), and the non-ionic surfactant, penta(oxyethylene) n-decyl ether ( $\text{C}_{10}\text{E}_5$ ), both aggregate at the interface between aqueous solution and several covalent solids. DDAPS forms spherical micelles on (hydrophilic) silicon nitride, spherical micelles on (hydrophilic) mica and hemicylindrical micelles on (hydrophobic) graphite.  $\text{C}_{10}\text{E}_5$  forms globular micelles on silicon nitride and flat sheets on graphite. Thus, both surfactants form lower curvature aggregates on a more hydrophobic substrate. This behavior is interpreted in terms of a lower free energy for the hydrophobic-substrate system when there is minimal contact between water and the hydrophobic substrate. Since the surfactant headgroups have a higher affinity for the hydrophilic substrates, there is also a correlation between the surfactant curvature and the affinity of the headgroup for the solid substrate. The aggregate morphology is not a function of surfactant concentration in the range investigated, but the repeat distance of the aggregate unit is a weak function of concentration. The effect of substrate hydrophobicity has been investigated for net-uncharged surfactants in order to exclude the effect of the strong monopolar charge-charge interactions which occur for anionic or cationic surfactants.

**504.E2****DYNAMIC SURFACE TENSIONS OF NON-IONIC  
SURFACTANT SOLUTIONS****Julian Eastoe<sup>1</sup>, James S. Dalton<sup>1</sup>, Philippe G.A. Rogueda<sup>1</sup>, Esther R. Crooks<sup>1</sup>,  
Alan R. Pitt<sup>2</sup> and Elizabeth A. Simister<sup>2</sup>**<sup>1</sup>*School of Chemistry, University of Bristol, Bristol BS8 1TS UK*<sup>2</sup>*Kodak European Research R. and D., Kodak Ltd., Headstone Drive, Harrow HA1 4TY, UK*

The air-solution equilibrium and dynamic surface tensions,  $\gamma_{\text{eq}}$  and  $\gamma(t)$ , of different non-ionic  $\text{C}_i\text{E}_j$  and glucamide surfactants have been studied as a function of concentration  $c$ , above and below their cmcs. DuNouy tensiometry was used to determine  $\gamma_{\text{eq}}$ , cmcs and the surface excesses  $\Gamma$ . The  $\gamma(t)$  decays were measured in the range 2ms  $\rightarrow$  12s using a maximum bubble pressure instrument, and analysed in terms of asymptotic solutions to the Ward and Tordai equation. At the start the  $\gamma(t)$  curves were all consistent with a diffusion-controlled adsorption. However, towards the end good evidence was found for a mixed mechanism with an adsorption barrier of between 5 and 12 kJ mol<sup>-1</sup>. This barrier does not seem to depend on the cmc,

surfactant type or the presence of micelles up to 100 x cmc. The results support theoretical predictions (Liggieri et al, J.Coll. Int. Sci. 156, 109(1993)) of the diffusion-activation adsorption kinetics for non-ionic surfactants.

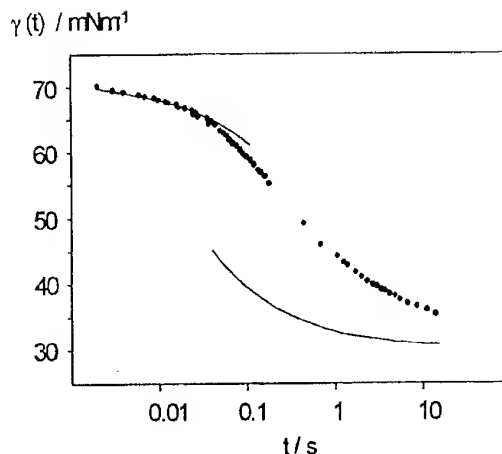
## 505.E2

### DYNAMIC SURFACE TENSIONS OF NON-IONIC SURFACTANT SOLUTIONS

Julian Eastoe and James S. Dalton

School of Chemistry, University of Bristol, BS8 ITS, UK

The air-solution equilibrium and dynamic surface tensions,  $\gamma_{eq}$  and  $g(t)$ , of different nonionic  $C_iE_j$  glucamide surfactant have been studied as a function of concentration  $c$ , above and below their cmcs. DuNouy tensiometry was used to determine  $\gamma_{eq}$ , cmcs, and the surface excesses  $\Gamma$ . The  $\gamma(t)$  decays were measured in the range 2 ms  $\rightarrow$  12s using a maximum bubble pressure instrument, and analysed in terms of asymptotic solutions to the Ward and Tordai equation. As shown right, at the start the  $\gamma(t)$  curves were all consistent with diffusion-controlled adsorption. However, towards the end good evidence was found for a mixed mechanism with an adsorption barrier of between 5 and 12 kJ mol<sup>-1</sup>. This barrier does not seem to depend on the cmc, surfactant type or the presence of micelles up to 100 x cmc. The results support theoretical predictions (Liggieri et al. *J. Coll. Int. Sci.* 156, 109 (1993)) of the diffusion-activation adsorption kinetics for non-ionic surfactants.



DST for  $C_{10}E_4$  below the cmc at  $5 \times 10^{-4}$  M (●)  
Lines are model calculations for short and long time limits

## 506.E2

### BREWSTER ANGLE AUTOCORRELATION SPECTROSCOPY: A NOVEL METHOD TO DETERMINE CHAIN TILT ANGLES IN AMPHIPHILIC SURFACE MONOLAYERS

Th.M. Fischer<sup>1</sup>, C. Lautz<sup>1</sup>, M. Weygand<sup>1</sup>, K. Kjaer<sup>2</sup>, M. Lösche<sup>1</sup>

<sup>1</sup>Institute of Experimental Physics I, University of Leipzig, Germany

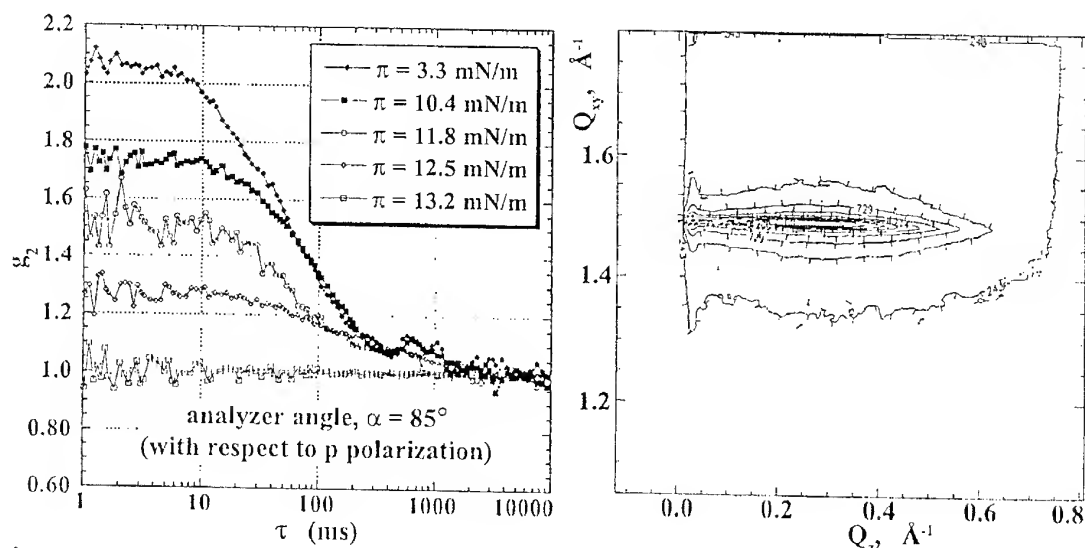
<sup>2</sup>Department of Solid State Physics, Riso National Laboratory, Denmark

Since the advent of Brewster angle microscopy (BAM) of organic monolayers on aqueous surfaces<sup>1,2</sup>, various efforts have been made to extract quantitative information from such images. In particular, attempts have been made to determine aliphatic chain tilt angles in Langmuir monolayers by analysing BAM micrographs<sup>3,4</sup>. In this approach, the contrast in the residual reflectivity of domains was evaluated that is brought about by different tilt azimuth directions with respect to the p-polarized incident light. Recently, Lautz et al. have introduced Brewster angle autocorrelation spectroscopy as a convenient tool to determine chain tilt angles in such systems<sup>5</sup>. This is a more direct method which is independent of the details of image processing. It utilizes the same effect by correlating the intensities from various domains floating through the area observed within the monolayer in the time course of the experiment. For a particular system, octadecanol on pure water, we have studied the development of the chain tilt angle while crossing the phase boundaries between the  $L_2$  phase and two different rotator phases<sup>6</sup>. In order to verify the validity of our approach, we have calibrated the BAM autocorrelation results with grazing incidence x-ray diffraction



(GIXD) experiments. The correspondence of the two different methods will be presented and the phase diagram of fatty alcohol monolayers on water will be discussed.

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BAM autocorrelation functions  $g_2$  (left,  $T = 20^\circ\text{C}$ ) and x-ray diffraction intensity contour plot ( $T = 19^\circ\text{C}$ ,  $\pi = 5.8 \text{ mN/m}$ , right) from octadecanol monolayers on  $\text{H}_2\text{O}$

## 507.E2 EFFECT OF SOLID SURFACE ROUGHNESS ON THE ADSORPTION FROM SOLUTION: NEUTRON REFLECTIVITY STUDIES FROM PARTIALLY LABELLED CATIONIC SURFACTANTS

G. Fragneto, R.K. Thomas, A.R. Rennie, J. Penfold

*Physical and Theoretical Chemistry Laboratory, Oxford, United Kingdom*

A neutron reflectivity study of the adsorption from aqueous solution of the cationic surfactant hexadecyltrimethylammonium bromide ( $\text{C}_{16}\text{TAB}$ ), at the CMC and below the CMC, on the hydrophilic surface of two silicon crystals is presented. The positively charged surfactant head-groups interact with the negatively charged silicon surface through electrostatic attraction while the chains tend to escape the aqueous environment so that the formation of bilayers of surfactant on the surface is expected. The two blocks used had different surface roughness and results of the adsorption at the two interfaces are compared, the difference being mainly related to the different roughness of the blocks. The surfaces were characterized before surfactant adsorption by measuring the neutron reflection at the silicon/water interface. By using selectively labelled surfactants a detailed description of the structure of the layer was obtained. The conclusions drawn are that a difference in roughness of about  $10 \text{ \AA}$  on the hydrophilic surfaces leads to an adsorbed amount of surfactant about 15% lower on the rougher surface. The thickness of the adsorbed layer is larger on the rough one. The symmetry of the bilayer is also affected by the roughness, being perfectly symmetrical on the smooth block and unsymmetrical on the rough one. The partially labelled surfactants (methylenes deuterated in groups of four) have proved to be particularly useful in the determination of this asymmetry. Results from all isotopic species confirm the formation of bilayers on the surface with a surfactant volume fraction less than one, so that water is found to be incorporated and the formation of islands (either flat or spherical) is postulated.

## 508.E2

## FORMATION OF DIMERS IN LIPID MONOLAYERS

**Theodor D. Gurkov***Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics Faculty of Chemistry,  
University of Sofia, James Bourchier Avenue 1, Sofia 1126, Bulgaria*

In this work we analyse theoretically the possibility of dimer formation in monolayers of zwitterionic lipids on hydrocarbon/ water phase boundary. Such layers, when compressed, are known to form condensed phases with different organisation and structure. Before this happens, i.e., at relatively large area per molecule, some small aggregates begin to form. We apply the van der Waals equation of state to interpret surface pressure/area ( $\Pi/A$ ) curves. A clear indication for existing of dimers is found [1]. The monolayer is modelled theoretically as an equilibrium mixture of monomers and dimers, taking into account the long- range interactions between the species. Statistical thermodynamics considerations allow us to find the composition of the surface layer, and the activity coefficients. The model contains three adjustable parameters: the equilibrium constant of dimerisation and the two interaction constants of type monomer-monomer and dimer- dimer. These quantities are determined from the best fit of  $\Pi/A$  data for five different temperatures. Very good agreement between the theory and other authors' experiments is observed. We conclude that the process of dimerisation is slightly exothermic, with a heat of about 2.5 kT per dimer. The interaction in the non- ideal layer is predominantly repulsive. Its energy has comparable magnitude to that of the dimerisation itself. As a consequence, the total heat effect in the real layer is observed to change sign, and to become positive, at low area per molecule. In these conditions the energy of the long- range repulsion is greater than the energy of dimerisation.

Our findings are consistent with a simple molecular model. It is known from the literature that net normal and lateral dipole moments can be assigned to the lipid polar heads. The normal dipoles give rise to overall repulsion between the species (the parameters in the equation of state, which are connected with integral long- range interactions, are negative). The lateral dipoles of the monomers supposedly rotate, and only at a small separation distance they can align antiparallel. The latter process leads to attraction and a dimer forms when two molecules approach closely.

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## 509.E2

MISCIBILITY OF HEPTANOL AND OCTYLSULFINYLETHANOL  
IN THE ADSORBED FILM AND MICELLE**Hidemi Iyota<sup>1</sup>, Takako Tomimitsu<sup>1</sup>, Makoto Aratono<sup>2</sup> and Kinsi Motomura<sup>2</sup>**<sup>1</sup>*Department of Life and Environmental Science, Kagoshima Prefectural Junior College,  
Kagoshima 890, Japan*<sup>2</sup>*Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka 812, Japan*

The surface tension of the aqueous solution of a heptanol and octylsulfinyethanol(OSE) mixture was measured as a function of the total molality of the mixture and the mole fraction of OSE in the mixture at 298.15 K under atmospheric pressure. The total surface density of heptanol and OSE and the mole fractions of OSE in the adsorbed film and micelle were evaluated numerically by applying the thermodynamic equations. The phase diagrams analogous to those of binary mixtures were drawn for the adsorption and micelle formation. Heptanol and OSE molecules were found to be miscible with each other in all proportions in the adsorbed film and partially in the micelle. Negative azeotropy of adsorption was observed; the total molality vs. mole fraction of OSE curves of the phase diagram of adsorption exhibit minima at which the mole fraction of OSE in the adsorbed film equals that in the solution. The azeotropy was ascribed to that heptanol and OSE are very similar in surface activity although their chemical structures are different from each other. Activity coefficients of heptanol and OSE in the adsorbed film were obtained by applying equations of the adsorption equilibrium to the curves of the phase diagram. Both values of the activity coefficients were less than unity and the excess Gibbs free energy of the adsorbed film was negative over the whole range of composition of the adsorbed film; the nonideality of mixing in the adsorbed film is ascribed

to that the attractive interaction of heptanol and OSE molecules in the adsorbed film is larger than those of the similar molecules. A large discrepancy in the mole fraction of OSE was observed between the adsorbed film and micelle coexisting in equilibrium at the critical micelle concentration. The discrepancy was ascribed to the large difference in size and property of head group between heptanol and OSE molecules.

## 510.E2 DETERMINING THE DYNAMIC INTERFACE TENSION OF SURFACTANTS

Karimov M.F., T.S. Phiet, N.V. Canh  
*"Vietsovetro" J. V., Vung Tau, Vietnam*

In this report, the method of determining the dynamic coefficient of interface tension is considered by "counter-droplet" instrument and this considers to the process of drop formation. Solving the problem of droplet, non-free system of material point-particle of ideal fluid is determined. The mass and volume of system are changeable values due to the increase in volume of droplet on time. The spherical configuration in the system is also considered. The changeable external forces in the system and reaction of droplet depend on the dynamic interface tension in the system. The available equation on analysis of dynamic coefficient of interface tension between interface, is a function of drop-formation time. The method of determining the dynamic coefficient of interface tension of surfactant solution is based on the results of 270 experiments with 16 types of surfactant solutions (ion, and non-ion type). Experimental results on determining the static and dynamic coefficient of interface tension of water based surfactant solution on the surface with air have been included within this study.

The experimental results show that the difference between them reaches to 50%

## 511.E2 EFFECT OF DYNAMIC STATE OF WATER-SURFACTANT-SOLID SYSTEMS ON ADSORPTION PHENOMENA

T.V. Karmazina  
*Institute of Colloid and Water Chemistry of National Academy of Science of Ukraine,  
 Kiev, pr. Vernadsky 42, 252680, Ukraine*

Investigation of adsorption phenomena in water-surfactant-solid systems is one of the central problem of colloid science. Modern experimental studies of interface phenomena in the system water-surfactant-solid at macrolevel as rule considering no changes that are occurring with the system components at microlevel have been carried out. An absence of information about microprocesses taking place in the system water-organic compound solid causes impossibility of deep understanding of mechanism of many adsorption process. The information about micro-process occurring at interface by investigation of the characteristics of the system dynamic state may be obtained. For the first time a new approach for investigation of adsorption process has been proposed - investigation of the effect of dynamic state of water-surfactant-solid system components on adsorption phenomena. The method of quasielastic slow neutron scattering has been proposed to obtain the characteristics of the dynamic state of systems. The effect of hydrophobic and hydrophilic sorbent on the dynamic state of water-surfactant systems has been investigated. The contact of solid sorbent with the system of water-nonionic surfactant leads to decrease of collective moving contribution (or the continuous mechanism of diffusion) in the system. As the concentration of nonionic surfactant in the system rises up to critical micelle concentration the characteristics of dynamic state of water-surfactant system after contact with hydrophobic sorbent are dramatically changed. That is the mechanisms of diffusion are redistributed due to the collective motions sharp decreases in water-surfactant system. A new conception of adsorption process according to which the change of the system water-surfactant components the dynamic state is the reason of colloid structure formation has been created. The changes of the dynamic state of water-surfactant systems under solid components are cause the different mechanisms of surfactant adsorption on hydrophilic and hydrophobic sorbents. The results obtained provide notice about the mechanism of dispersed system stability; they explain existence of wide variety of shapes of

isotherms of surfactant adsorption and mechanism of formation of different adsorption structures on solid. The investigation of the effect of dynamic state of water-surfactant-solid system components on adsorption phenomena may contribute to more deep understanding of the adsorption process and to development of colloid science.

## 512.E2 EFFECT OF SOLID SORBENTS ON DYNAMIC STATE OF WATER-SURFACTANT SYSTEMS

T.V. Karmazina<sup>1</sup>, V.I. Slisenko<sup>2</sup>, N.A. Klimenko<sup>1</sup>

<sup>1</sup>*Institute of Colloid and Water Chemistry of National Academy of Science of Ukraine, Kiev, Ukraine*

<sup>2</sup>*Institute for Nuclear Research of National Academy of Science of Ukraine, Kiev, Ukraine*

The characteristics of dynamic state of water-(nonionic, cationic) surfactants systems before and after contact with solid (graphite carbon black and silica gel) has been investigated. The characteristics of dynamic state (the overall diffusion coefficients, the contribution from single- or Frenkel and multi- or Lagrange particles motions and lifetimes of vibrational state) of molecules was obtained by quasielastic slow neutron scattering data. Note that the experimental quasielastic neutron scattering data (dependencies of broadening on the square of the transferred momentum) characterise the overall diffusion of hydrogen-containing molecules, their fragments, micelles and the cluster of both water and surfactant. That is the contribution from Lagrange particles motions to the overall mechanism of diffusion originates from the surfactant molecules with bound water molecules, as well as from the clusters of water. This contribution corresponds to the mechanism of continuous diffusion. The contribution from the single-particle motions according to Frenkel to the overall diffusion coefficient reflects the dynamics of individual molecules and their fragment and corresponds to the jump-wise mechanism of diffusion. It has been shown that the contact of water-nonionic surfactant system with hydrophilic and hydrophobic sorbents promotes redistribution of the diffusion mechanism of the molecules. As the concentration of nonionic surfactant (Triton X-100) in aqueous solution rises up to critical micelle concentration, the mechanism of diffusion after contact solution with solids dramatically changes because the contribution from multiparticles motions (or the continuous mechanism of diffusion) becomes less important. The changes of the dynamic state in water-nonionic surfactant systems under solid are the cause of the origin of the different colloid structures. The changes of the dynamic state water-(hexadecylpyridinium bromide) surfactant under carbon black are not significant. The dependencies of the critical micelle concentration displacement under solid were quantitatively estimated. After contact of water with silica gel and carbon black no changes of dynamic state of water have been established in our experiment.

## 513.E2 INVESTIGATION OF THE TILT ANGLE BEHAVIOR IN THE PHASE DIAGRAM OF OCTADECANOL BY BREWSTER ANGLE AUTOCORRELATION SPECTROSCOPY

C. Lautz, and Th.M. Fischer

*Institute of Experimental Physics I, University of Leipzig, Germany*

With Brewster angle autocorrelation spectroscopy (BAS)<sup>1</sup> we have developed a method for quantitative measurements of the aliphatic chain tilt angle in Langmuir monolayers. Compared to the common method of grazing incidence X-ray diffraction (GID)<sup>2</sup>, which needs high intensity X-ray sources, BAS requires a relatively simple experimental setup feasible in a standard laboratory. The time duration to measure one tilt angle is only three minutes.

For octadecanol on pure water we have investigated the tilt angle behavior on definite places in the phase diagram of this system. The structure of molecular packing in the different phases in the phase diagrams of long chain alcohols on the water surface was investigated by Shih et al.<sup>3</sup>. At higher pressures there are three untilted phases, where the S and the LS(Rot I) are distorted hexagonal, however the LS(Rot II) is undistorted hexagonal. In the only tilted L<sub>2</sub> phase the aliphatic chains are tilted toward their next

nearest neighbor. The phase transitions from the tilted to the untilted phases are of first order for the LS(Rot I) phase and of second order for the other untilted phases. The tilt angle behavior in the vicinity of the triple points (S/LS(Rot I)/L<sub>2</sub>) and LS(Rot I)/LS(Rot II)/L<sub>2</sub>) in the phase diagram shows some surprising effects. Near the triple points we found strong changes of the tilt angle behavior within the L<sub>2</sub>' phase in a small temperature region indicating a first order phase transition. However, this transition cannot neither be induced on isobaric heating nor cooling due to strong super cooling and super heating effects. The quantitative behavior of the tilt angles at the two definite regions in the phase diagram will be discussed.

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## 514.E2 POLYDISPERSE SURFACTANTS AT THE SOLID/LIQUID INTERFACE: AN ELLIPSOMETRIC STUDY

L. Luciani, R. Denoyel

*Centre de Thermodynamique et Microcalorimétrie, 26 rue du 141 RIA, 13003 Marseille, France.*

The adsorption of anionic and nonionic polydisperse surfactants was studied by ellipsometry on titania and silica, respectively. The effect of polydispersity is mainly observable in the low concentration range. In the case of polyethoxylated nonionic surfactant adsorption on silica, the long chain components are preferentially adsorbed at low concentration. Ethoxysulphated surfactants do not adsorb on silica in the same conditions (pH>3). Their ethoxy chains seem to have no interaction with the titania surface at pH 2.5 where adsorption is mainly due to an electrostatic interaction between sulphate head and positive sites of the surface. At saturation, surface concentrations and thicknesses of the adsorbed layer lead to the same interpretations as those deduced from results obtained on powders with the same surfactants or on flat surfaces with monodisperse surfactants: the surface seems to be covered with aggregates of limited extension whose thickness is comparable to micelle diameter. It is also worth noticing that the linear evolution of apparent areas per molecule with ethoxy number is very similar for nonionic and anionic sets.

## 515.E2 PEO-PPO SURFACTANTS IN AQUEOUS SOLUTIONS CONTAINING A HYDROTROPIC AGENT

Claudia R.E. Mansur<sup>1</sup>, Clara M.F. Oliveira<sup>1</sup>, Elizabete F. Lucas<sup>1</sup>, Gaspar González

<sup>1</sup>*Instituto de Macromoléculas Prof. Eloisa Mano/UF RJ, P.O. Box: 68525, Rio de Janeiro, Brazil*

<sup>2</sup>*Petrobrás Research Center (CENPES), Rio de Janeiro, RJ, Brazil*

Poly(ethylene oxide-b-propylene oxide) (PEO-PPO) copolymers are classified as nonionic surfactants. In aqueous solutions, these copolymers form aggregates called micelles and are able to solubilize water-insoluble compounds and adsorb at interfaces. In this work, the solution behavior of the PEO-PPO diblock copolymers coupled with hydrocarbons groups ( $M_n \approx 600-1200$  and EO/PO ratios  $\approx 0.36-1.5$ ) was studied in the presence of the hydrotropic agent, sodium p-toluenesulfonate (NaPTS). The CMC (critical micelle concentration) values were obtained from surface tension measurements, U.V. absorption of an oil-soluble dye [1,4-bis(isopropylamino) anthraquinone] and viscometry data. Differential scanning calorimetry measurements were used to obtain estimated values of the micellization enthalpy. Figures 1 and 2 show the results obtained from surface tension measurements.

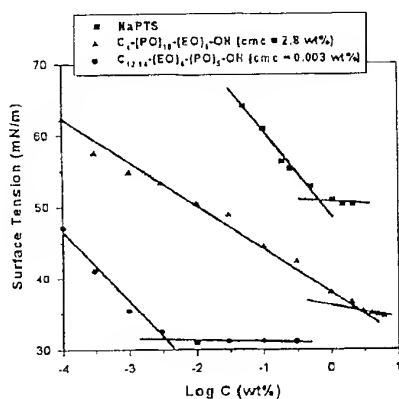


Figure 1. Surface tension as a function of copolymer or NaPTS aqueous solutions concentrations, at 30°C

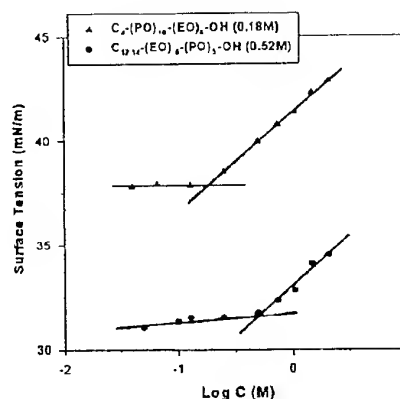


Figure 2 Surface tension of the copolymers solutions (1 wt%) as a function of NaPTS concentration, at 30°C.

It is observed in Figure 1 that, as expected, the compounds adsorb and reduce the solution surface tension until the surface become saturated. The CMC values are related to the solubility of the copolymers. Figure 2 shows the opposite behavior: at 1 wt% copolymer concentration and increasing the NaPTS concentration, the surface tension remains constant until the aggregates of NaPTS start forming. Beyond this concentration surface tension increases. These results may be ascribed to interaction between the copolymer and the hydrotrope in bulk resulting in a reduction of the free surfactant concentration in solution or to adisplacement of the surfactant from the interface by the hydrotropemolecules. The concentration of NaPTS aggregation depends on the copolymer structure and composition. The CMC values determined from dye solubilization and viscometry data agree with these results. The micelle formation was also verify using DSC and an exotherm "phase transition" was observed. The enthalpies of micellization were obtained and it was observed that copolymer coupled with C<sub>12-14</sub> presents higher enthalpy value than that coupled with C<sub>4</sub>.

The authors would like to thank the financial support from CNPq, CAPES, CEPG-UFRJ and FINEP.

## 516.E2

### INTERFACIAL BEHAVIOUR OF IONIC SURFACTANTS ADSORPTION FROM EQUIMOLAR SOLUTIONS OF ANIONIC AND CATIONIC SURFACTANTS

Krystyna Medrzycka, Elzbieta Lamparska

Technical University, Chemistry Faculty, Narutowicza 11/12, 80-952 Gdansk, Poland

The study of the anionic and cationic surfactants adsorption from their mixtures is of considerable interest, both for theoretical and practical reasons. For example, the ionic surface active agents adsorption is of great importance in the process of oil removal by coagulation or flotation from O/W type emulsion. Depending on the type of ionic surfactant the charge of oil droplets and air bubbles reaches positive or negative value. It is known, that the barrierless flotation is possible when the charge of both surfaces is close to zero. To achieve such conditions the concentration ratio of anionic surfactant to cationic surfactant should be close to 1. In this connexion the investigation on coadsorption of anionic and cationic surfactants at the air/water and oil/water interfaces were undertaken.

The following surfactants were used:

anionic: sodium n-decyl sulfonate and sodium n-dodecyl sulfonate,  
cationic: decyltrimethylammonium bromide, dodecyltrimethylammonium bromide.

As an oil phase decane was used.

Surface tension and interfacial tension isotherms were obtained by using the drop-weight and drop-volume methods.

Gibbs surface excess values for surface active cations and surface active anions was calculated. The composition of the interfacial films for equimolar aqueous solutions of anionic and cationic surfactants was found. It was stated that the composition of the interfacial films is nonequimolar. Besides, it was found that

the asymmetry for films at the air/water interface is different from that for films at the decane/water interface. The inorganic salt content influences the asymmetry of the surface film as well.

## 517.E2

### NEW THERMODYNAMIC MODELS FOR SURFACTANT ADSORPTION ISOTHERMS

R. Miller<sup>1</sup>, V.B. Fainerman<sup>2</sup>, A.V. Makievski<sup>1,2</sup> and R. Wüstneck<sup>3</sup>

<sup>1</sup>MPI for Colloids and Interfaces, Rudower Chaussee 5, D-12489 Berlin, Germany

<sup>2</sup>Institute of Technical Ecology, 25, Boulevard Shevchenko, Donetsk, 340017, Ukraine

<sup>3</sup>University of Potsdam, Institute of Solid State Physics, Rudower Ch. 5, D-12489 Berlin, Germany

Thermodynamic models are proposed which allow to take into consideration new findings on the structure of soluble surfactant adsorption layers. This belongs in particular to the idea that molecules can undergo orientational changes in an adsorption layer due to increasing surface coverage and thus surface pressure. In addition, two-dimensional aggregation in an adsorption layer can be assumed when the interaction between the surfactant molecules is sufficiently large. Classical models used in literature so far were unable to consider these effects adequately. Only very recently, first attempts have been made to include these effects specifically into surface tension isotherms and equations of state, such as in the models by Lin in 1991 or by Lunkenheimer in 1992.

The proposed thermodynamic models are based on the Butler equation. This is a generally accepted relationship for the chemical potential of a surfactant at an interface which includes the surface work of a molecule at an interface. The general basis of the model allows to consider different cases, i.e. ideal and non-ideal adsorption layers with changing molecular area, 2D-aggregation, mixtures of surfactants.

A first simple model allows to describe the change of the partial molar area  $\omega$  for adsorbed molecules depending on the degree of saturation of the adsorption layer. Equations are derived for an adsorption isotherm and a surface tension isotherm of a single surfactant or of a surfactant mixture. The model assumes that each molecule may adsorb in two different states, i.e. with a large area  $\omega_1$  at smaller surface pressures  $\Pi$ , and a smaller  $\omega_2$  at larger surface pressures  $\Pi$ . The transition is governed by the principle of Braun-Le Chatelier. Surface tension data for N-n-hexadecyl-N,N-dimethylammonio acetic acid bromide at the interface air/solution are used as an example to demonstrate the application of the theory. The experimental results are in good agreement with the model.

Another model is derived for surfactant molecules capable to form two-dimensional aggregates in the adsorption layer at a liquid/fluid interface. Equations for an adsorption isotherm and a surface tension isotherm are derived for the case of different molecular area demand of a free surfactant molecule or an aggregated molecule in the adsorption layer. Experimental surface tension data for different surfactants, for example decanol or sodium dodecyl sulphate, are compared with the theory. For instance the decanol data are in good agreement with the model when a dimer formation in the adsorption layer is assumed.

## 518.E2

### THE CONDITION OF LOOSENING IN THE STRUCTURE OF CELLULOSE WITH SURFACE-ACTIVE SUBSTANCES (SAS)

I. Ossovskaya, G. Poltoratsky and I. Strelugina.

St. Petersburg State Technological University of Plant Polymers, 4, ul. Ivana Chernykh,  
198092 St. Petersburg, Russia

An attempt has been made to study the possibility of loosening for the submicroscopic structure of cellulose under the influence of SAS (PL-64, B-V-32, procsanol). The change of the sorption ability of the cellulose was characterized by the methods of the sorption of the direct green three-azoic color, of the sorption of water vapor and by the heat of the wetting. It is shown, that SAS fixed on the cellulose by weak forces of the sorption do not cause any strong change of the internal surface of the polymer. However, their activating action is considerably revealed in a number of treatments (by way of illustration, in the interaction with NaOH). It is shown that  $R$  increases of the heat effect, when the treated cellulose interacts with alkali, is

connected with a change of the surface energy condition on the phase division boarder-line under the influence of SAS. It is stated that the action of SAS on the cellulose structure is different depending on the NaOH concentration and on the SAS origin, with the maximal increase of the enthalpy ( $\Delta H$ ) are appeared in the region of concentrations which correspond to the maximum of solubility and swelling of cellulose in NaOH.

**519.E2****ON THE ADSORPTION OF SODIUM OLEATE AT THE  
MERCURY/ELECTROLYTE INTERFACE USING DIFFERENTIAL  
CAPACITANCE MEASUREMENTS**

**Nikos Papadopoulos and Antonis Avranas**

*Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki,  
54006, Thessaloniki, Greece*

The interfacial behavior of sodium oleate adsorbed on a hanging mercury drop electrode has been investigated by means of the concentration dependence of the differential capacity using phase sensitive ac voltammetry. The reconstruction of C vs E curves, sampled after many phase-sensitive ac chronoamperometric experiments until the attainment of the equilibrium permits a detailed study of the adsorption phenomena. The shape of these curves allows an estimation of the structure of the layer of oleate anions adsorbed at the electrode surface. Sodium oleate molecules that aggregate to form association structures in solution, strongly bond onto the electrode surface under the influence of the electric field into surface aggregates which depend on their concentration and the applied potential. At negative polarizations a surface film of aggregates starts to develop which at premicellar concentrations, according to surface tension data, is likely to be monolayer. The appearance of a capacitance well at positive polarizations is attributed to the formation of a polylayer. The central capacitance pit with a very low capacitance value most probably corresponds to a condensed state of the interface. The bulk micelles in the positive region are desorbed from the interface. A strong dependence is observed on the adsorption phenomenon upon time.

**520.E2****SURFACTANT SORPTION FROM AQUEOUS SOLUTIONS  
ON TITANIUM-CONTAINING SORBENTS**

**O.I. Pendelyuk, V.V. Strelko, N.A. Yaroshenko**

*Institute of Sorption and Endoecology of the National Academy of Science of Ukraine, 30/32 Shelkovichnaya  
st., Kiev 252024, Ukraine*

It have been studied the sorption of plain surfactant (sodium ethylbenzenesulfonate) and micelle-generating surfactant (chlorid hexadecylpyridinium - HDPCl) from the aqueous molecular solutions on the titanium-containing sorbents. The following nonporous sorbents have been used: titanium dioxide and titardum dioxide modified with phosphorus-acid anion, and also mesoporous titanium-manganese sorbent.

The adsorption isotherms of surfactants have been determined by the conventional method of constant sorbent load and the constant degree of surfactant removal of solution. It has been established that the HDPCl isotherms on the nonporous sorbents are of a double-stage type. On the first stage of adsorption saturation, a monomolecular layer is formed in which hydrophilic surfactant groups are chemisorbed on the surface of titanium dioxide, and hydrophobic radicals are oriented into a solution volume. On the second stage of adsorption saturation, the surface associates are formed.

The studies of HDPCl adsorption on mesoporous titanium-containing sorbent have shown that thei isotherm form is close to a such one for the system aqueous solution of surfactant-activated carbon but, on surfactant adsorbility the mesoporous titanium-containing sorbent surpasses the activated carbon.



**521.E2****THE SURFACTANT ADSORPTION ON  $\text{TiO}_2$   
IN THE PRESENCE OF WATER****Polunina I.A., Mikhailova S.S.***Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia*

The influence of water contained on the surface of  $\text{TiO}_2$  and in the toluene solutions of stearic acid (SA), octadecylamine (ODA) and octadecyl alcohol (ODAI) on the surfactants adsorption on titania surface was investigated. It was found that water (5% pigment weight) hinders the chemisorption of SA from toluene due to the reversal of the surface carboxylation reaction in the presence of water and partial blocking of the surface rutile sites by water molecules adsorbed on rutile or, transferred to its surface from the liquid phase as a result of their incomplete solubilization by surfactant molecules in solution. The chemisorption of ODA from toluene-water emulsion was the same as under anhydrous conditions. ODA molecules proved to be the most competitive among the surfactants investigated, and displacing water from the surface, they form strong chemical bonds with rutile.

The observed increase in physical adsorption of SA and ODA from emulsions may be associated with some ionization of the surfactant molecules as a result of their association with water molecules.

No chemisorption of ODAI was detected, its physical adsorption, leading to complete modification of the entire surface, is somewhat reduced in the presence of water on account of blocking of the surface sites by water molecules. A condition of implementation of the chemisorption of ODAI is the complete removal of water from the system, both the water present and reaction water.

**522.E2****THEORETICAL MODELLING OF LANGMUIR MONOLAYERS****F. Schmid, C. Stadler, H. Lange***Johannes Gutenberg Universität Mainz, D55099 Mainz, Germany*

We study a coarse grained, continuum model for Langmuir monolayers by self consistent field theory and by Monte Carlo simulations. Amphiphilic molecules are represented by stiff chains of monomers with one end grafted to a planar surface. The resulting phase diagram is discussed and the different phases are characterized with respect to their density profiles, collective tilt, distribution of chain defects etc. In particular, we discuss the origin of successive fluid-fluid transitions, the possible origins of tilt order and the factors which determine the direction of tilt.

**523.E2****SURFACTANT EXCHANGE DYNAMICS OF ADSORPTION LAYERS  
INVESTIGATED BY PFG-NMR DIFFUSION****Monika Schönhoff, Olle Söderman***Physical Chemistry 1, Chemical Center, University of Lund, Box 124, S-22100 Lund, Sweden*

The equilibrium dynamics of the exchange of surfactants between an adsorption layer and bulk solution are investigated for the nonionic polyethyleneoxide surfactant  $\text{C}_{12}\text{EO}_5$ . The surfactant is adsorbed on polystyrene latex spheres dissolved in water, surfactant molecules therefore occur in three different sites, i.e. monomers, micelles and adsorbed surfactant, which exhibit different diffusion coefficients.

NMR diffusion experiments using pulsed field gradients (PFG) and a stimulated echo sequence are performed. It was found that on variation of the experiment time scale by changing the gradient pulse spacing,  $\Delta$ , the transition from slow to fast surfactant exchange, as compared to  $\Delta$ , can be covered. Assuming exchange between micelles and monomers to be fast and considering both as one "bulk" site, the region of intermediate exchange is described by a two-site model of exchange-coupled diffusion.

Diffusion experiments were performed for several surfactant concentrations with varying gradient spacings. The data were fitted to the model resulting in the average residence time of the surfactant in the monolayer and in bulk solution, resp. The stability of the fits was checked in Monte-Carlo simulations of the experimental noise, resulting in improved error intervals for the fitted parameters. Residence times are in the

range of 10 ms, where the residence time of surfactant molecules in the bulk is increasing and that in the monolayer is decreasing with surfactant concentration.

## 524.E2 STRUCTURE OF FLUID INTERFACES: ELLIPSOMETRIC STUDIES AND INTERFACIAL TENSIONS OF SIMPLE AND COMPLEX LIQUID MIXTURES

Jens Schulz, Gerhard H. Findenegg

Iwan N Stranski Institute of Physical and Theoretical Chemistry,  
Technical University Berlin Strasse des 17. Juni 112, D-10623 Berlin, Germany

The liquid/liquid-interface in two-phase systems of simple and complex liquid mixtures, specifically n-hexane+perfluorohexane, water+monoethyleneglycolmonoisobutylether (i-C<sub>4</sub>E<sub>1</sub>) and water + diethyleneglycolmonopentylether (C<sub>5</sub>E<sub>2</sub>)+perfluoroheptane, was investigated using optical ellipsometry and interfacial tension measurements. Ellipsometric studies of a binary mixture of near-critical composition close to its critical solution point at which the two coexisting phases ( $\alpha$  and  $\beta$  become identical (*critical* interface), can elucidate the intrinsic structure and the effect of capillary waves for this type of I/I-interface. Ellipsometric measurements were also performed for the I/I-interface between a near-critical binary mixture (water+C<sub>5</sub>E<sub>2</sub>) and an inert external spectator phase, e.g. perfluoroheptane (*semicritical* interface). For both types of interface the temperature dependence of the ellipticity can be represented by a scaling function for the intrinsic composition profile, using independent measurements of the correlation length  $\xi$  and the refractive indices of the coexisting phases. The roughness of the I/I-interface due to capillary waves is also considered in the quantitative analysis of the experimental ellipticity. The temperature dependence of the interfacial tension of *critical* interfaces exhibits the predicted scaling behaviour, whereas for a *semicritical* interface the tension exhibits no significant temperature dependence up to the lower critical solution point of the water-amphiphile mixture.

## 525.E2 INTERACTIONS IN SURFACTANT/POLLUTANT/SOIL MINERAL SYSTEMS

M. J. Schwuger and E. Klumpp

Institute of Applied Physical Chemistry, Research Centre Jülich, D-52425 Jülich, Germany

Surfactants alter the sorption properties of soil minerals by means of ion exchange, surface hydrophobing and expansion of silicate layers (swelling clays). Consequently they influence the sorption of hydrophobic organic pollutants (HOCs) and their transport in soils and sediments. Depending on the mechanisms of interaction synergistic and antagonistic effects may be observed.

An overview of the influences of different surfactants on the sorption of HOCs (phenols, benzene derivatives, pesticides) from dilute aqueous solutions on soil minerals is given. The interactions depend strongly on the surfactant as well as on the mineral structure. They are discussed in terms of ad- and desorption isotherms, basal spacings by X-ray diffraction and the kinetics of sorption.

In mixed pollutant/surfactant systems, cationic and nonionic surfactants enhance the sorption of HOCs on clay minerals significantly at concentrations below the CMC (synergism) in contrast to anionic surfactants showing antagonistic effects at low concentrations. Data obtained from desorption, X-ray and kinetic experiments permit additionally the understanding of the sorption mechanisms.

## 526.E2 ELECTROKINETIC BEHAVIOUR OF MACROPOROUS GLASS MEMBRANES IN IONIC SURFACTANT SOLUTIONS

M. Sidorova, L. Ermakova, I. Savina

Sankt-Petersburg State University, Sankt-Petersburg, Russia

The electrokinetic potentials and surface conductance were measured for the porous glass membranes (PG) with pore radii 66 and 160 nm in solutions containing a specifically adsorbing counterion

(cetylpyridinium,  $CP^+$ ) and coion (dodecylsulfate,  $DS^-$ ). It was established that the specific adsorption of  $DS^-$  coions in a neutral pH range did virtually not change the surface conductance of PG and led to an increase in the  $|\xi|$  electrokinetic potential at  $C > 3 \cdot 10^{-3}$  M. A decrease in pH of the solution led to an increase in the specific adsorption of  $DS^-$  ion and to higher (than for NaCl solutions)  $|\xi|$  values at  $pH < 6$ . The specific adsorption of  $CP^+$  counterions caused the reversal of the  $\xi$  - potential sign and the isoelectric point corresponded to  $C_{IEP} = 2,3 \cdot 10^{-4}$  M. The dependences of the efficiency coefficient and the specific surface conductance on the concentration of the cetylpyridinium chloride solution showed the minima at the isoelectric point. The same influence of ionic surfactant solutions on the electrokinetic potential and specific surface conductance was found for quartz glass surface (plane disc and fibers).

## 527.E2

### POLYMERIC SURFACTANTS AS STABILIZERS FOR EMULSIONS AND SUSPENSIONS

Th.F. Tadros

*ICI Surfactants, Everberg, Belgium*

Polymeric surfactants of the ABA block and  $BA_n$  graft type are ideal systems for stabilization of emulsions and suspensions. In this lecture, I will discuss the application of an ABA block copolymer, where A is polyhydroxy stearic acid and B is polyethyleneoxide (PEO) for preparation of water-in-oil emulsions. Interfacial and rheological measurements illustrated the performance of the block copolymer at the w/o interface, as well as the bulk properties of the emulsions. The  $BA_n$  graft copolymer with B being polymethyl methacrylate and A being PEO was also applied for preparation of concentrated suspensions. Adsorption and rheological studies were used to illustrate the performance of this polymer at the solid/liquid interface.

## 528.E2

### EFFECTIVITY OF DETERGENTS IN DYNAMIC SURFACE CLEANING

A. Timmerman and G. Frens

*Laboratory for Physical Chemistry, Delft University of Technology, Delft, The Netherlands*

*Introduction.* The washing of textile can be characterized empirically by the 'Sinner-factors': energy, temperature, chemistry and time. Departing from these factors the washing process can be optimized. If, however, the backgrounds of the Sinner factors are known, it will be possible to optimize the washing process from a more fundamental point of view. From earlier research it was concluded that a soiled textile could never be cleaned in a normal washing process if the most important mechanism governing the mass transfer from fabric to detergent solution were diffusion. Therefore, in this research it is supposed that there is a flow both along the fabric-surfactant solution interface and in the fabric yarns.

*Theory.* At high surfactant concentrations a surfactant bilayer is formed between the flowing liquid and the surface of the hydrophilic yarn. During the washing process fabrics are moved and deformed continuously. By stretching the fabric, liquid (the surfactant solution) is squeezed from pores in the yarns. This makes the second surfactant layer flow along the fabric-liquid interface. This flow along the interface may be advantageous for the effectivity of the washing process by causing local supersaturation in the bilayer, which gives rise to instabilities. These instabilities can cause a motion perpendicular to the textile surface.

*Experimental.* It is envisaged that under certain temperature and pH conditions highly concentrated solutions (about 3 times the critical micelle concentration) can form bilayers at a hydrophilic surface of a capillary. If concentrated surfactant solutions will flow more quickly through this capillary than diluted solutions, this indicates a slip condition at the wall of the capillary. In order to find evidence for flow along the liquid-fabric interface, surfactant solutions of different concentrations are pushed through narrow capillaries of different lengths and diameters. The flow through the capillary is measured as a function of hydrostatic pressure. If non-linear effects in the pressure-flow curve are a function of concentration, instabilities at the fluid textile interface are present.

## 529.E2

SURFACTANTS ADSORPTION ON AMORPHOUS  
TITANIUM PHOSPHATE

O.Ya. Uryupina, S.S. Mikhajlova and N.V. Serebryakova

*Institute of Physical Chemistry, Russian Academy of Sciences, Leninskij prosp. 31,  
Moscow, 117915 Russia*

There are still few papers dealing with the processes involved in the interaction of surface active substances with amorphous titanium phosphate.

In this connection the mechanism of cation- and anionactive surfactants (octadecylamine, quaternary ammonium base Alkamon, and stearin acid) interaction with amorphous titanium phosphate has been studied by the authors of this presentation.

The direct adsorption values measurements as well as Fourier Transform Infrared spectroscopy of several gaseous test-molecules have been employed to evaluate the influence of water and solvent nature on surfactant interaction processes.

Amorphous titanium phosphate, obtained at 500 K, has been used in the course of this work.

The occurrence of active sites of different nature (highly acidic isolated P-OH groups, i.e. Brønsted acid sites; Lewis sites; amphoteric Ti-OH groups) has been demonstrated.

It was shown that:

1. Cation-active surfactants interact with the acid P-OH groups, the proton being captured, as well as realize the use of the lone pairs of the coordination with  $Ti^{5+}$  sites.

2. Anion-active surfactants interact with Lewis sites, surface compounds similar to carboxylic acid salts being formed; at the same time surface species hydrogen bonded to Ti-OH groups could be formed.

3. Amine adsorption wasn't influenced by the presence of water in adsorption systems. On the contrary, physical as well as chemical adsorption of stearin acid was diminished strongly by it.

4. Values of maximum adsorption of all the surfactants from the polar solvent ethylcellosolve was reduced as compared to values of irreversible adsorption from non-polar solvent toluene. It is the formation of ester-type compounds proceeding in the course of titanium phosphate-ethylcellosolve interaction and their subsequent partial adsorption on titanium phosphate surface, that could be the cause of this effect.

## 530.E2

NONIDEAL MIXING IN ADSORBED FILM AND MICELLE OF  
IONIC-NONIONIC SURFACTANT MIXTURESMasumi Villeneuve<sup>1</sup>, Norihiro Ikeda<sup>2</sup>, Takanori Takiue<sup>1</sup>, Kinsi Motomura<sup>1</sup>, and Makoto Aratono<sup>1</sup><sup>1</sup>*Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812-81, Japan*<sup>2</sup>*Faculty of Human Environmental Science, Fukuoka Women's University, Fukuoka 813, Japan*

Ionic-nonionic surfactant mixture systems were investigated by means of surface tension measurement. The surface tension of the aqueous solutions was measured as a function of the total molality and composition of the surfactants and analyzed by our thermodynamic procedure. Phase diagrams were drawn to manifest the relation of compositions between the bulk solution and the adsorbed film or the micelle and that between the micelle and the adsorbed film. To evaluate interaction between the surfactants quantitatively, we defined activity coefficients and excess Gibbs energy of mixing, where dissociation of the ionic species is taken into account, in the adsorbed film and the micelle.

The total molality and the composition of surfactants are defined by the following equations:

$$m = 2m_1 + m_2 \quad (1), \quad X_2 = m_2 / m \quad (2)$$

The measurement was done at 298.15 K under atmospheric pressure and the experimental error was within  $\pm 0.05 \text{ mN m}^{-1}$ .

One example of the systems investigated is that of dodecylammonium chloride (DAC) -octyl methyl sulfoxide (OMS) mixture. The phase diagram of micelle formation is shown in Fig. 1 and the excess Gibbs energy of mixing in the micelle is estimated and plotted against the composition in the micelle  $X_2^M$  in Fig. 2. With the aid of the excess Gibbs energy, deviation from the ideal mixing is estimated to be negative over the entire composition range with a minimum value of about  $-0.8 \text{ kJ mol}^{-1}$ . Miscibility of surfactants in the adsorbed film and the micelle is discussed also in the other systems from the viewpoints of phase diagrams, the activity coefficients, and the excess Gibbs energy.

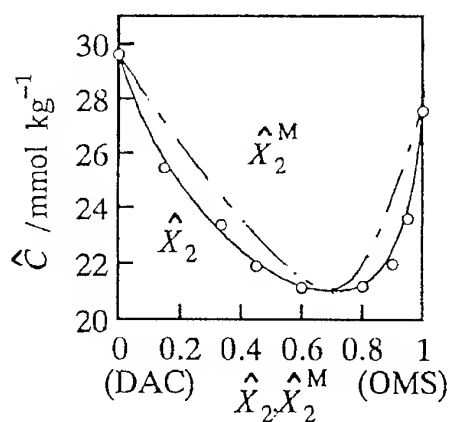


Fig.1 Phase diagram of micelle formation

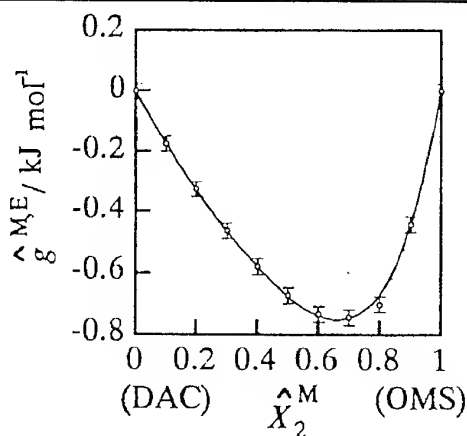


Fig.2 Excess Gibbs energy in micelle

**531.E2****SURFACE AGGREGATION OF AN ANIONIC SURFACTANT  
ON GRAPHITE IN THE PRESENCE OF ADDED ELECTROLYTE**

Erica J. Wanless\* and William A. Ducker

*Department of Chemistry, University of Otago, Dunedin, New Zealand**\*current address: Department of Chemistry, University of Newcastle, Newcastle, Australia.*

The aggregated structure of sodium dodecylsulfate (SDS) adsorbed to the graphite-solution interface has been determined using Atomic Force Microscopy (AFM). The SDS adsorbs in periodic structures when the solution concentration is in the range 2.8 to 81 mM. Using previously obtained adsorption isotherms, we deduce that these structures are hemicylindrical. The period of the surface aggregates decreases when the concentration of SDS is increased due to a decrease in the surfactant headgroup repulsions, and approaches the diameter of bulk micelles at high concentration ( $\sim 5$  nm).<sup>1</sup>

In the presence of NaCl, similar hemicylindrical surface aggregates are also formed. Once again, the period decreases as the concentration of NaCl is increased, and is proportional to the solution Debye length. We propose that this is a result of a decrease in inter-aggregate spacing rather than a decrease in aggregate size.

No change in phase was observed on addition of  $\text{MnCl}_2$ . When  $\text{MnCl}_2$  is added at constant low SDS concentration, the period also decreases linearly with solution Debye length down to a limiting period of about 5 nm. At surfactant concentrations several times greater than the cmc, the addition of divalent ions has no observable effect on the adsorption.

1. Erica J. Wanless; William A. Ducker, *J. Phys. Chem.*, 1996, 100, 3207-3214.

**532.E2****THE MODEL OF ADSORPTION OF IONIC SURFACTANTS  
AT THE AIR/SOLUTION INTERFACE. COMPARISON WITH THE SURFACE TENSION  
AND SURFACE POTENTIAL ISOTHERMS OF SODIUM DODECYL SULPHATE**P. Warszynski<sup>1</sup>, W. Barzyk<sup>1</sup> and K. Lunkenheimer<sup>2</sup><sup>1</sup> *Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Kraków, Poland*<sup>2</sup> *Max Planck Institut für Kolloid und Grenzflächenforschung, Berlin-Adlershof, Germany*

Adsorption of ionic surfactants is strongly influenced by the electric properties of the air/solution interface. However, the theoretical description of all electrical phenomena occurring at the interface during the adsorption of ionic surfactants is complicated and still far from being complete. The combination of measurements of the surface tension and surface potential at the solution interface can provide necessary information to develop and verify any model of the adsorption.

A model of the adsorption of ionic surfactants at the solution/air interface has been developed. The model is based on the assumption of the interdependent adsorption of the surfactant ions and counterions in the inner (Stern) layer at the solution/air interface. The electric potential drop in the electric double layer is calculated according to the Guy-Chapman model for the diffuse double layer and modified Stern model for the inner layer with the corrections for the discrete charge effects. The electric charge at the interface originates from the difference of the adsorption of surfactant ions and counterions in the Stern layer. The total potential drop at the interface is assumed to consist of two contributions:

- i. the negative potential drop in the compact and diffuse double layers as described above.
- ii. the potential drop due to the effective dipole moment of the adsorbed surfactant molecules, assumed positive, attributed mainly to the terminal hydrocarbon group.

Surface potential ( $\Delta V$ ) of free surface of Na-n-dodecyl sulphate (SDDS) solutions in distilled water was measured using the vibrating plate method. Surface tension measurements were performed for the same solutions with Du Nouy ring method. Prior to the measurements, the SDDS solutions were carefully purified in the automatic purification apparatus to obtain the state of "surface chemical purity".

The surface potential isotherms,  $\Delta V$  vs.  $\lg c$ , obtained for the SDDS solutions exhibit a pronounced minimum. Basing on the Gibbs adsorption equation it can be concluded that the minima occur just within the concentration range corresponding to the transition from the Henry region to one typical for the adsorption of most amphiphiles at free solution surface at high surface coverage.

Our model correctly describes the dependence of the surface tension and surface potential on the SDDS concentration in solution. In particular the experimentally observed minimum originates from the competition of negative contribution to the potential drop due to the adsorbed surfactant and counterion charges at the interface and the positive contribution from the effective dipole moment of the hydrocarbon chains.

### 533.E2

#### RETARDATION OF OXYGEN DIFFUSION TO WATER BY SURFACTANT MONOLAYERS

S. Yapar, S. Peker

*Ege University, Chemical Engineering Department Bornova, Izmir, Turkey*

The use of surfactants in many industrial applications and households induces serious problems of water pollution. The oxygenation of the pollutants by the dissolved oxygen in water is one of the major factors which could be affected by the presence of surfactant monolayer. In this investigation, the retardation effect of the monolayer was investigated.

The diffusion experiments were carried out in a diffusion cell. The Clark type oxygen electrode ("Schott- Geräte, Germany) was inserted into the cell and the liquid film  $0.246 \pm 0.017$  mm in thickness was formed on the electrode surface.

During the experiments, the concentration of oxygen at the bottom of the film was recorded in certain time intervals. The oxygen concentration in the cell was kept constant by letting air flow over the liquid film. Flow rates were kept low (1-2 ml/min) through the cell to avoid wave formation at the surface of the film.

The oxygen concentration at the bottom surface increases after a while (~100 s) in the presence of surfactant in contrast to a sudden increase in the case of pure water. This effect was attributed to the surface resistance of the adsorbed surfactants and formation of  $O_2$  sinks within the micellar structure.

### 534.E2

#### METHOD OF CONSTANT DEGREE OF SURFACTANT REMOVAL FOR THE STUDY OF ADSORPTION FROM SOLUTIONS

N.A. Yaroshenko, A.V. Dymanskii

*Institute of Colloid and Water Chemistry, Ukrainian National Academy of Science,  
Pr. Vernadskii 42252680, Kiev, Ukraine*

The studies on adsorption of the soluble surfactant on the solid sorbents are performed predominantly by a conventional method of the constant sorbent load. The experimental points in such the

adsorption isotherms are not equivalent, i.e., they have a different degree of surfactant's removal ( $C_f$ ) of solution: 95-10%. Herewith, for the numerous systems, it is impossible to establish experimentally the initial linear section of isotherm from which the constant of system adsorption equilibrium is calculated. As a result, in the research area of surfactant adsorption from solutions on the solid sorbent, many incongruences have been accumulated.

The author proposed to measure surfactant equilibrium adsorption at constant  $C_f$  that provides to obtain comparable results both for the members of homologous row and for different sorbents. The characteristic feature of the method consists in the fact that sorbent loads are increased in line respecting to the initial (and equilibrium) concentrations of surfactant solution. After that as the stable equilibrium condition in system is attained, the amount of adsorbed substance is calculated according the equation of conventional method. For the plotting of adsorption isotherm, the results of experiments with a certain  $C_f$  (+/- 2%) value are chosen.

The author studied various systems - aqueous solution of surfactant - solid sorbent, using the conventional and proposed methods. It is shown that the second method has such the advantages: identity (equality) of experimental points on adsorption isotherm; the initial linear section of isotherm is not extrapolated but measured; scientifically grounded and adjustable determining all the adsorption parameters; the stable values of thermodynamic parameters; the possibility to research the effect of solid phase concentration on the adsorptive interaction in any system: surfactant solution - solid sorbent.

## 535.E2      ADSORBED LAYERS OF IONIC SURFACTANTS AT AQUEOUS SOLUTION- PERFLUORODECALIN INTERFACE

N.M. Zadymova, Z.N. Markina

*Department of Chemistry, Moscow Lomonosov State University, Moscow, Russia*

Using a tensiometric method ( $\pm 0.1$  mN/m), surface activity, adsorption and state of equilibrium adsorbed layers of sodium dodecyl (SDS) and tetradecyl (STS) sulfates at the aqueous solution - perfluorodecalin interface have been investigated at 293 K. Perfluorodecalin (PFD) was selected as the nonpolar phase because of its low cohesive energy density, high oxygen solubility, and its efficiency for the production of blood substitutes. The effect of the nature of a nonpolar phase on the surface activity  $\Gamma$  of ionic surfactants, the standard free energy of adsorption,  $\Delta G^0$ , and the increment of the standard chemical potential  $\Delta \mu_m^0$ , required for the methylene group to be transferred from water to a nonpolar interface was studied for highly diluted aqueous solutions of SDS and STS at the air, perfluorodecalin, and octane interfaces under adsorption equilibrium. For expanded adsorbed layers (under extremely low surface occupancy degree  $\theta \rightarrow 0$ , Henry's region) of SDS and STS at the interface with PFD, in contrast to the water-octane interface, a marked effect of the nonideal mixing of hydrocarbon radicals of adsorbed diphilic ions with perfluorodecalin molecules was observed. The surface activity of the ionic hydrocarbon surfactants in aqueous solutions is higher at the interface with the liquid which is better ("more ideally") mixed with hydrocarbon radicals of the adsorbed diphilic ions. A state equation describing the behaviour of an investigated ionized monolayers at the aqueous solution - PFD interface in wide range of  $\theta$  has been found. An important role is shown to be played by the effect of the nonideal mixing of hydrocarbon radicals of adsorbed diphilic ions with PFD molecules at  $0 < \theta < 1$ .

## 536.E2      THE INTERACTIONS OF SATURATED FATTY ACIDS AT THE DODECANE/WATER INTERFACE AND THEIR SODIUM SALTS AT THE AIR/WATER INTERFACE

Włodzimierz Zwierzykowski, Donata Konopacka - Lyskawa

*Chemical Faculty, Technical University of Gdansk, Gdansk, Poland*

The fatty acids and their soaps are applied in many detergent, cosmetic and technical preparations and a major part of them is present in industrial and domestic sewage. They have an amphipathic structure, so they accumulate at interfaces and have a strong tendency to form micelles in solutions as well as to interfere

with processes in the ecosystems. Therefore the properties of fatty acids and fatty acids soaps films at the oil/water and at the air/water interfaces are very interesting and important.

In this study the results of investigations on adsorbed films of lauric, myristic, palmitic and stearic acids at the dodecane/water interface and their corresponding sodium soaps at the air/water interface are present. The interfacial tensions at the interface between dodecane solution of fatty acids and water and between aqueous solutions of fatty acid sodium salts and air were measured using the Du Noüy (ring) method. On the basis of these results the standard free energies of adsorption ( $\Delta G_{\text{ads}}^0$ ) and of micellization ( $\Delta G_{\text{mic}}^0$ ) of the above mentioned compounds were calculated in the investigated systems. The dependence of the standard free energy of adsorption ( $\Delta G_{\text{ads}}^0$ ) on the interface coverage ( $\theta$ ) was determined from the Langmuir isotherm and the interactions of surfactant particles at corresponding interfaces were discussed.

### 537.E3 FLUORESCENT DYES AS MODEL "HYDROPHOBIC MODIFIERS" OF POLYELECTROLYTES: A STUDY OF POLY(ACRYLIC ACIDS) LABELED WITH PYRENYL AND NAPHTHYL GROUPS

D.F. Anghel<sup>1</sup>, Françoise M. Winnik<sup>2</sup>, V. Alderson<sup>2</sup>, Y. Morishima<sup>3</sup> and M. Mizusaki<sup>3</sup>

<sup>1</sup>Department of Colloids, "I.G. Murgulescu" Institute of Physical Chemistry,  
Spl. Independentei 202, 77208 Bucharest, Romania

<sup>2</sup>Department of Chemistry, McMaster University, 1280 Main St. West, Hamilton,  
Ontario, Canada L8S 4M1

<sup>3</sup>Department of Polymer Chemistry, Osaka University, Osaka, Japan

Studies on fluorescently-labelled polymethacrylic or polyacrylic acids were reported by Chu and Thomas [1], and Turro and Arora [2], respectively. In both cases they obtained the polymers by copolymerization of methacrylic or acrylic acid and a dye-substituted monomer. We report here the synthesis and characterization of labeled polyacrylic acid (PAA) obtained by postmodification of a commercial sample (PAA of  $M_w \sim 150,000$ ). The polymer was prepared by a simple amide formation procedure, modeled after a technique previously used to prepare PAA based associative thickeners. The reaction between the polyacid and an arylalkyl amine was performed in an aprotic solvent, N-methylpyrrolidone, in the presence of dicyclohexylcarbodiimide. Polyacrylic acids labelled with pyrene, naphthalene, and with both chromophores, were prepared starting with 1-pyrenylmethyl amine, 4(1'-pyrenyl)butyl amine, and 1-naphthylmethyl amine. Characterization by GPC and NMR confirmed that the dye was linked covalently to the polymer. The amount of fluorophore incorporated was determined by UV spectroscopy, and it ranged in between 0.5 and 3.0 molar %. Photophysical properties of the labeled polymers were determined in aqueous and nonaqueous media. In water, the labeled polymers exhibit characteristic polyelectrolyte properties, their behavior being strongly dependent on pH and ionic strength. However, the incorporation of hydrophobic chromophore induced subtle changes, in polymer properties which will be emphasized during the presentation.

1. D.Y. Chu and J.K. Thomas, *Macromolecules*, 17 (1984) 2142

2. N.J. Turro and K.S. Arora, *Polymer*, 27 (1986) 783.

### 538.E3 EFFECT OF POLYMERIC INTERACTIONS ON THE STABILITY OF FUNCTIONAL EMULSIFIER-FREE ACRYLATE LATEXES

T. Aslamazova

*Institute of Physical Chemistry of Russian Academy of Sciences, Moscow, Russia*

The influence of functional comonomers of varying degrees of water solubility and containing groups capable of forming crosslinked structures on the stability of emulsifier-free acrylate latexes has been studied. Stability of the particles was estimated in terms of electrostatic and structural forces of their interactions. A decrease in stability of the latexes with an increase in hydrophobicity of functional comonomers was demonstrated to correlate with a drop of zeta-potential of particle surface and with an increase in coefficient of structural forces of attraction. Hydrophilic functional comonomers improve the



stability of particles in comparison with an unmodified system due to a decrease in the structural forces and an increase of electrostatic forces of particles repulsion.

### 539.E3 MICELLIZATION IN WATER AND ADSORPTION ONTO SOLID PARTICLES OF BLOCK COPOLYMERS

A. Jada, J. Hoffstetter, B. Siffert and P. Dumas

*Institut de Chimie des Surfaces et Interfaces, 15 rue Starcky, B.P. 2488,  
F-68057 Mulhouse Cedex, France.*

Micelle formation and adsorption at  $\text{TiO}_2$ -solution interface of a series of PS-PEO block copolymers in aqueous solutions were studied using fluorescence probing and small angle X-ray methods. Further the stability of aqueous  $\text{TiO}_2$  dispersion in the presence of the copolymers was investigated by micro-electrophoresis, optical density and sedimentation measurements. The dissolution of pyrene as fluorescent probe in aqueous surfactant solutions leads to slow and rapid decreases of the  $I_1/I_3$  ratio, as the copolymer concentration increases,  $I_1$  and  $I_3$  are respectively the intensities of the first and the third vibronic peaks in the pyrene fluorescence emission. This behavior was due to the characteristics of the copolymer and/or to the copolymer association efficiency in water. Moreover the adsorption at the plateau level increases with decreasing PEO chain length. The zeta-potential of  $\text{TiO}_2$  particles decreases with increasing copolymer concentration and reaches a plateau value. Stable suspensions were obtained when appreciable zeta-potential values resulted. Finally stabilization using block copolymers was more effective with samples having higher weight fractions of PS block.

### 540.E3 SYNTHESIS, CHARACTERIZATION AND ASSOCIATIVE PROPERTIES OF WATER SOLUBLE POLY(ACRYLAMIDES) WITH TRIBLOCK STRUCTURES

Pierre Lebreton<sup>1</sup>, Philippe Gramain<sup>1</sup>, Bernard Boutevin<sup>1</sup>, Christian Collette<sup>2</sup>,  
Jean Marc Corpart<sup>2</sup>, Gilbert Garcia<sup>2</sup>

<sup>1</sup>*Hétérochimie Moléculaire et Macromoléculaire - CNRS - Ecole Nationale,  
Supérieure de Chimie de Montpellier - 8, rue de l'Ecole Normale, 34296 Montpellier cedex 5 - France*

<sup>2</sup>*Centre d'Application de Levallois - Elf-Atochem- Levallois-Perret - France*

Hydrophobically modified poly(acrylamides) were synthesized by radical polymerization of acrylamide with an azo-initiator bearing hydrophobic groups. Polymerizations were conducted in a precipitant medium (acetonitrile) and led to surfactant-polymer like structures, typically  $\text{R}_{\text{F,H}}\text{-PAM-R}_{\text{F,H}}$ , with hydrophobic perfluoro-segments ( $\text{R}_{\text{F}} = \text{C}_8\text{F}_{17}\text{-}$  or  $\text{R}_{\text{H}} = \text{C}_{16}\text{H}_{33}\text{-}$ ) located at each end of the hydrophilic polymer chain (PAM). Triblock and diblock ( $\text{R}_{\text{F}}\text{-PAM}$ ) structures were formed. However, the amount of triblocks rises to 85% by increasing the amount of initiator from 0,05% to 7% (mol/mol based on monomer). These results can be interpreted in terms of predominancy of primary radical recombination.

GPC experiments conducted in mixed eluants ( $\text{H}_2\text{O}/\text{MeCN}$ ) prove that our modified poly(acrylamides) contain both diblock and triblock populations, held responsible for the bimodal distributions in water elution. In water, triblocks associate in aggregates eluting as monodisperse entities with high apparent molecular weights ( $\text{Mw} \sim 10^5\text{-}10^6$ ,  $I=1,1$ ). Diblocks elute later separately. By addition of acetonitrile in the mobile phase, aggregates dissociate progressively into isolated coils until, they disappear completely. There remains then only one peak with 30% acetonitrile ( $\text{Mw} \sim 10^4$ ,  $I=2,5$ ), corresponding to simultaneous elution of triblocks and diblocks.

Based on GPC results, triblocks and diblocks were successfully separated from the rough polymer by using a fractionation technique. Each population was characterized by GPC as before, showing the associative properties of the triblocks. The functionality was calculated by combining fluorine content with average number molecular weights (determined in non-associative elution conditions).

Rheological studies in water using a CARRI-MED CSL100 rheometer demonstrated the associative properties of the triblocks in contrast to the diblocks. Furthermore, their viscosifying properties were compared on the basis of their molecular weights ( $\text{M}_w$ ), ranging between 10000 and 60000.

Finally, these modified poly(acrylamides) were investigated as additives in fire-fighting aqueous foams, and proved to be of great interest. Triblocks can also be used as associative thickeners in painting.

### 541.E3     HYDRATION OF A SHORT CHAIN POLY(OXYETHYLENE) ( $C_1E_2C_1$ ) STUDIED BY ANALYSIS OF THE O-H RAMAN BAND

Zh.S. Nickolov<sup>1</sup>, N. Goutev<sup>1</sup>, G. Georgiev<sup>1</sup> and H. Matsuura<sup>2</sup>

<sup>1</sup>Department of Quantum Electronics, Faculty of Physics, Sofia University,  
5, J Bouchier Bul., 11 64 Sofia, Bulgaria

<sup>2</sup>Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama,  
Higashi-Hiroshima 739, Japan

The hydration of the short chain polyoxyethylene  $C_1E_2C_1$ , has been studied in the range of concentrations up to 0.3 mole fraction (m.f.) by Raman scattering. Simultaneous curve fitting of the OH and CH isotropic Raman bands has been employed to decompose them into components. The parameters of the main components of the water OH band at about 3200 and 3400  $\text{cm}^{-1}$  have been analysed to extract information about the hydration structure of the solution.

The results from this study show that there are two interesting regions of enhancement of the hydrogen bond structure in the solution at low concentrations up to 0.11 m.f., which can be connected with the existence of two different hydration structures. In the first of them around 0.03 m.f. the water structure is stabilised due to the simultaneous effect of hydrophobic hydration around the methylene groups and the  $\text{CH}_3$  end groups from one side, and hydrogen bonding at the sites of the ether oxygens of the POE molecules, from the other. The prevailing  $C_1E_2C_1$  molecules with gauche conformation have a maximum relative concentration at around 0.02 m.f. [1] and we assume that their favourable incorporation in the water network is the reason for the strengthening of the H-bond structure in this region. In contrast, the second type of hydration structure around 0.11 m.f. can be explained with the build up of a most compact homogeneous hydrogen bond network in which  $C_1E_2C_1$  molecules are interconnected with direct hydrogen bonds with most water molecules and the effect of hydrophobic hydration is diminished. This is the maximum enhancement in the H-bond structure of the solution and agrees well with the observed maximum values of the sound velocity at 0.085 m.f. [2] for the same system.

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2. H. Matsuura and K. Fukuhara, *Bull. Chem. Soc. Jpn.*, 59, 763 (1986).

### 542.E3     MOLECULAR MECHANISMS OF THE DEMIXING PHENOMENA IN THE AQUEOUS SOLUTIONS OF POLYMERS

A.V. Oleinikova<sup>1</sup>, L.V. Brovchenko<sup>2</sup>

<sup>1</sup> Kiev Taras Shevchenko University, Ukraine,

<sup>2</sup> Institute of Physics, Kiev, Ukraine

Consolute phenomena in the aqueous solutions of the polymers are considered in view of the temperature induced structural changes of the hydrogen bonding water and functional groups of polymer. One strong H-bond between single water molecule and functional group provides creation of the water-like cluster, containing dozens water molecules. Existence of the two H-bonds between single water molecule and functional group leads to the creation of the organic-like cluster, containing only a few water molecules. Water-like clusters provide better embedding of the solute molecule in the structure of the liquid water and have strong tendency to self-assembly. At some "critical" concentration water-like cluster merge all together, water-rich phase extracts from the solution and therefore phase separation takes place. As far as the water-like clusters have in general higher energies and more possible configurations in comparison with organic-like ones, temperature dependence of their concentration possesses maximum at some temperature. The intersections of this domelike dependence with the line of "critical" concentrations correspond to the lower and upper consolute points.

Analysis of the demixing phenomena in aqueous solution of polymer is based on the consideration of the polymer molecule as set of the functional groups, acting in H-bonds with water [1]. At first approximation one water molecule per one functional group may be considered and the temperature dependence of the concentration of the water-like clusters, averaged over all functional groups of polymer, is used for the comparison with experimental results.

The proposed model is applied to the well investigated aqueous solution of polyethylene glycol, which possesses in general case closed-loop phase diagram [2,3]. The double critical point corresponds to the molecular weight  $M = 2140$ . Increasing of  $M$  and addition of the salt NaCl leads to the appearance and extension of the immiscibility gap, where two phases coexist. Polyethylene glycol consists of the two main kind of the functional groups: ethereal oxygen atom groups and the hydroxyl end group, besides weak H-bonds of water with methylene groups of the polymer chain were taken into account. The atom-atom potentials method was used in order to calculate temperature dependence of the water-like clusters. Variations of  $M$  change ratio between the numbers of the ethereal oxygen atoms and hydroxyl groups in polymer. Addition of salt changes the strength of the H-bonds between water and polymer molecules. Both these factors influence concentration of the water-like clusters and results in the shifts of the critical temperatures.

The experimentally observed changes of the absolute values of the lower and upper critical consolute temperatures are reproduced quantitatively in the framework of the proposed cluster model of demixing.

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2. S. Saeki, N. Kuwahara, M. Nakata, M. Kaneko, Polymer, 17, 685 (1976).
3. S. Saeki, N. Kuwahara, M. Nakata, M. Kaneko, Polymer, 18, 1027 (1977).

### 543.E3

#### STUDY OF THE $M^+$ , $M^{2+}$ EXCHANGE ON A CHARGED POLYELECTROLYTE

I. Pochard, P. Couchot, A. Foissy

*Laboratoire d'Electrochimie et des Systèmes Microdispersés (LESM),  
16, route de Gray F-25030 Besançon France*

The comprehension of polyelectrolytes adsorption requires a full knowledge of polymer/counterions interactions. In the case of anionic polyions for instance, divalent cations induce a significant increase of adsorption, well above that expected as a consequence of ionic screening. Specific effects of counterions are also observed in cations series, i.e. alkali or alkaline earth cations do not similarly influence adsorption. Calcium, for example is much more effective than magnesium to induce adsorption of polyacrylic acid. Actually, the interactions between a polyelectrolyte and cations being in the solution change the conformational and electrostatic features of the polyion and then modify the adsorption properties of the polyion.

Our study aims to characterize the  $M^+$ ,  $M^{2+}$  / polyacrylic acid (PAA) interactions in relation to their contribution in the adsorption process.  $M^+$  ions are successively the cations of the alkali serie, i.e. lithium, sodium and potassium ions and  $M^{2+}$  ions are either barium ions or calcium ions.

Experimental techniques include potentiometric analyses of the polyacrylic acid ionisation with various alkali hydroxide in presence of different support electrolytes. Ionic Selective Electrode (ISE) and conductometric analyses are employed to quantify the binding of cations on PAA. Finally, microcalorimetric measurements are carried out to evaluate the variation of enthalpy which accompanies the  $M^+$ ,  $M^{2+}$  exchange onto the polyion.

Although it is well known that monovalent ions like alkali ions don't interact specifically with polyacrylic acid, it is pointed out here that the  $M^+$ ,  $M^{2+}$  exchange on PAA depends on the nature of  $M^+$ . Nevertheless, the divalent cations studied are strongly complexed by polyacrylic acid and a sufficient concentration of these ions leads to the total remove of monovalent ones.

### 544.E3 IMPROVEMENT OF COHESIVE AND ADHESIVE PROPERTIES OF GLOBULAR PROTEINS

A.A.C.M. Rutten, M.C. van der Leeden and G. Frens

*Laboratory of Physical Chemistry, Delft University of Technology, Delft, The Netherlands*

A network of macromolecules is necessary to create a strong cohesion within a glue layer. The large flexible random coil chains which are able to deform in an elastic way, make it possible to deform the adhesive layer without breaking the bonds. That is supposed to be the reason that up till now only polymers and proteins with a flexible random coil structure have been used in the making of adhesives. The disadvantage of a random coil polymer is that it can not adsorb to a substrate without losing entropy. Rather than being flattened and lose entropy, the coils keep themselves at a coil's radius distance away from the surface. They leave an empty 'depletion' layer, and pure solvent fills the empty space. For a good adhesion the depletion effect must be overcome by a stronger polar attraction between the material in the surface and the segments of the polymer resulting in adsorption.

Unlike synthetic polymers, a natural protein is rarely dissolved as a random coil. The shape and structure of globular protein molecules is very specific, and highly organized because of strong "polar" interactions between the side groups of the amino acids. A globular protein is "highly non-ideal", i.e. unlike a random coil, in the terminology of polymer solutions. The strong structure of an unmodified globular protein does not much help for cohesion strength. However, the specific bonds which shape the molecule can be broken by denaturation, after which the protein structure becomes more like the random coil of synthetic polymers. Strong adhesion can then be reached if there is enough polar attraction between protein coil segments and the substrate to overcome the depletion effect. In a protein there are all kinds of different polarities, charges and sizes of the side groups. Under all circumstances there will be some of the segments of the chain which have a high polar affinity for the surface. This makes the polypeptide chain of the proteins highly interesting for colloidal applications in adhesives.

Our aim is to achieve knowledge about the cohesive and adhesive properties of globular proteins and to improve these properties by denaturation realized by changing the solvent quality and/or the temperature. As model for our study we use the globular protein  $\beta$ -lactoglobulin. This is the most important protein in whey. Since the production of whey (a waste product of cheese making) still increases, it is for environmental and economical reasons profitable to develop a new application for proteins of this kind.

Circular dichroism spectroscopy shows the effect of different solvents upon the secondary structure of  $\beta$ -lactoglobulin. In these experiments the parameters like pH, dielectric constant and the ability of the solvent to accept or donate electrons have been varied. The ability of a solvent to interfere with the intramolecular hydrogen bonds of the globular protein molecule, is probably the most important parameter of the solvent to transform the protein into a random coil structure. Measurements of the intrinsic viscosity of  $\beta$ -lactoglobulin in different solvents confirm these results. Adsorption experiments give more insight in the effect of the unfolding of the globular protein.

### 545.E3 STRUCTURE OF HIGHLY CHARGED SEMI-DILUTE POLYELECTROLYTE SOLUTIONS

O. Safi<sup>1,\*</sup>, F. Lafuma<sup>2</sup> and C.E. Williams<sup>3,1</sup>

<sup>1</sup>LURE, CNRS-CEA-MESR-University of Paris-Sud, bât 209 D, 91405 Orsay, France

<sup>\*</sup>Present address: CEA-SI3M-17 rue des Martyrs, 38054 Grenoble, France

<sup>2</sup>Laboratoire de physico-chimie des polymères, CNRS-Paris VI-ESPCI-10 rue Vauquelin,  
75231 Paris, France

<sup>3</sup>Physique de la Matière Condensée, CNRS-Collège de France-11 place Marcelin Berthelot,  
75231 Paris, France

We show experimentally that the structure properties of highly charged polyelectrolyte solutions are dominated, not only by electrostatic interactions, but also by hydrophobic interactions which are not usually taken in to account in the theoretical models.

For instance, the behaviour of aqueous solutions of an hydrophilic polyelectrolyte at intermediate charge density  $f$ , such as Poly (acrylamide-co-sodium-2-acrylamido-2-methyl propane sulfonate) (AMAMPS) obey to the Manning condensation law. The structural properties of the AMAMPS solutions determined by small angle X-ray and neutrons scattering (SAS), show qualitative agreement with the theoretical predictions of an isotropic transient network of semi flexible chains.

However, the behaviour of a highly charged hydrophobic polyelectrolyte, above the condensation threshold, such as copolymers of styrene-co-styrene sulfonate (PSS), above the condensation threshold, don't obey to the Manning-Oosawa condensation law; the effective charge decreases as the charge decreases. The structural properties of the PSS solutions investigated by SAS depend on the charge content. Also, the existence of hydrophobic domains, more important that the charge density is lowered, has been evidenced by fluorescence emission spectroscopy.

Finally, it is proposed that the structure of the PSS solutions evolves from a conformation of semi rigid chains forming an isotropic network, for the highly charged polyelectrolytes, to a more compact state as the charge density is lowered, to reach finally the globule conformation, for the less charged PSS ( $f \approx 30\%$ ).

### 546.E3 THERMAL FLUCTUATIONS OF HYDRATED BIOMACROMOLECULES AND THE MÖSSBAUER SPECTRA PARAMETERS

**T.Yu. Tchesskaya and A.V. Zatovsky**

*Department of Theoretical Physics, I.I. Mechnikov Odessa State University,  
Dvoryanskaya 2, 270 100 Odessa, Ukraine*

At present the dynamic properties of macromolecules are successfully studied by the methods of Mössbauer absorption spectroscopy (MAS) and Rayleigh scattering of Mössbauer radiation (RSMR). The parameters of the Mössbauer spectra are essentially influenced by the temperature and hydration. The internal mobility of macromolecules increases with these factors. As a result, the observed spectral line peaks differ from Lorentzians. The interpretation of the experiments usually bases on models in which proteins are represented by special mechanical constructions. These models are able to explain the temperature dependence of the spectra. However, there are no analytical calculations describing the effects of hydration on the protein globule dynamics. In this work, a model of the thermal fluctuations of the fragments composing the globule is proposed. The macromolecule is modeled by a porous permeable particle containing a fluid. This particle is immersed in another fluid. The dynamic properties of the water associated with the macromolecule fragments are described by the linearized Debye-Brinkman equation. The collective oscillatory motions of the particle constituents are in the general case described by optical and acoustic spectra. We are interested in the low-frequency excitations of proteins corresponding to the macromolecule conformational dynamics due to small changes of the mean positions of the groups of atoms. These low-frequency thermal motions can be described in terms of the classical hydrodynamics as deformations of a visco-elastic medium. The collective motion of the particle fragments is taken into account through the dynamic variables determining the shape of the globule surface that is assumed to be close to spherical. The temporary behavior of the dynamic variables satisfies the Langevin equations with random sources of external forces. Inside the globule the water is rigidly bound to its fragments. The mass and friction coefficients are found solving the auxiliary problem concerning the excitation of fluid flows inside and outside the globule. The model describes the dependence of the RSMR and MAS spectral parameters on hydration. The time correlation functions of the local flow velocity and the corresponding local diffusion coefficients were calculated. These quantities depend on the permeability coefficient and the position of the Mössbauer atom inside the globule. The hydration coefficient is determined by means of a combination of the mass coefficient for porous particles with fluid and the mass coefficients in two limited cases: the fully "frozen" flow inside the particle and the opposite case of a viscous drop. The results of numerical calculations have shown a considerable contribution of the oscillations in the low-frequency region of the spectra. We have compared the obtained results on the hydration dependence of the RSMR spectra parameters and the Lamb-Mössbauer factor with the experiments on hydrated macromolecules from the literature.

**547.E3 MICELLAR STRUCTURE OF WATER-SOLUBLE POLYELECTROLYTES****L.I. Tertykh and Ye.F. Rynda***A.V. Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine,  
42 Vernadsky Blvd., 252680 Kiev-142, Ukraine*

The investigation of water-soluble polyelectrolytes structure and their colloido-chemical modification are very significant for formation of an elective electrophoretic coatings. The purpose of this work consists in the study of colloido-chemical properties of polymerized and polycondensed film-forming materials used as water-soluble varnish paint binders for electrodeposition. The wide range of water polyelectrolyte solutions with different concentrations including ones used for electrodeposition was investigated. The concentration dependencies of specific conductivity, density and viscosity indicate the presence of four critical micelle concentrations (CMC). We have shown the possibility of differential spectrophotometry application to determine all CMC values and it is of particular importance for concentrated polyelectrolyte solutions. Breaks on the curve of concentration dependence, received by this method, conform to values achieved by traditional methods of CMC determination. Differential spectrophotometry method can also be used to determine CMC of non-ionic and ionic surfactants. The presence of CMC numerosity in concentrated polyelectrolyte solutions for electrodeposition indicates the existence of micelles in different shapes that indirectly was confirmed by light scattering method. Apparently, considerable colloid solubility of hydrophobic substances (n-nonane, toluene, benzene etc.) in concentrated solutions of carboxyl-containing oligomers is connected with plate micellae formation. High solubilizing ability (up to 16% mass) of polyelectrolytes gives possibility for purposeful modification of these film-forming materials to produce coatings with different properties. Besides, polyelectrolytes for electrodeposition stipulate high dispersion stability (more than a month period) where different modifying additives (including pigments) are dispersed phase. Therefore, the data set concerning the properties of polyelectrolytes investigated confirms that they appeared to be colloid surfactants with various shapes of micellae.

**548.E3 THE INTERPHASE BOUNDARY FORMATION AT THE PHASE  
DECOMPOSITION IN DIFFUSION GRADIENTS IN BINARY POLYMER SYSTEMS****Alexander I. Zagaytov***Institute of Physical Chemistry RAS, Moscow, Russia*

For the first time, the interphase boundary formation at diffusion zones phase decomposition in binary polymer systems were observed by means of optical interferometry method. For systems under consideration (polystyrene-decalin, polystyrene-cyclohexane, polybutadiene-ethers of ftaeic acid) the concentration and temperature dependencies of interaction parameter, location of binodal and spinodal curves were calculated. Stable, metastable, labile solution areas and location of phase reversing boundary are defined on the evaluated generalised phase states diagrams.

It has been shown, that when passing through a critical temperature ( $T_{crit}$ ), the process of phase decomposition in preformed at  $T > T_{crit}$  diffusion zone is accompanied by an instant formation of the *plane interphase boundary*, which is coincided with contour of polymer phase. Its temperature and concentration location corresponds to area of phase reversing on the phase states diagram. In accordance with downturn of temperature ( $T \ll T_{crit}$ ), zones of nucleation (I) and spinodal (II) decomposition are formed close to the phase boundary. The interphase boundary location remains constant in time, but the main morphological changes occur in the areas I and II. This process leads to traditional interphase boundary formation, which separates two areas with composition corresponding to coexisting phase. It has been shown that similar structures appear in adhesive polymer composites being characterised by phase state diagrams with UCTS.

Being based on the thermodynamic theory of solutions and phenomenological diffusion theory, the generalised model of mass-transfer processes in a binary polymer system has been designed. The proposed theoretical model allows forecasting the space arrangement and kinetic of diffusion zones changes at phase decomposition which are in good agreement with experimental data.

### 549.E3 INVESTIGATION OF THE INTERACTION OF POLYETHYLENE OXIDE WITH METAL CATIONS IN WATER MEDIA

I.V. Zhivkova, A.M. Zhivkov, D.S. Stoychev

*Institute of Physical Chemistry, Bulgarian Academy of Science, 1113 Sofia, Bulgaria*

The viscosimetric technique is employed in the study of the electrostatic behaviour of polyethylene oxide (PEO) in water solution. It is found that PEO behaves as a polyelectrolyte though by chemical structure it is a nonionic polymer. This is explained by the possible binding of the polymer chain with impurity ions.

Photon-correlation spectroscopy technique is employed in the study of adsorption of the PEO on the surface of  $\gamma$ - $\text{Al}_2\text{O}_3$  particles. The surface charge of the particles is altered by the medium pH. A difference in the polymer adsorption on positively and negatively charged surface is established. A conclusion is drawn that in water medium PEO macromolecules bear an electric charge, the sign of which is positive. It is assumed that the effect observed results from the PEO binding to certain cations in the medium.

The impurity content is estimated with X-ray microprobe and atomic-absorption analysis. The study of commercial PEO specimens indicates that the main impurity ion is Ca. The electrical conductivity measurement of PEO water solutions gives reason to believe that Ca exists mainly in the form of dissociated  $\text{CaCO}_3$ . An assumption is presented that  $\text{Ca}^{2+}$  bind with the oxygen atoms of the ethylene oxide groups, attributing a positive electrical charge to the polymer chain. This conclusion can be spread also over polyethylene glycol (the low molecular analogue of PEO).

### 550.E3 FLOW AND ADSORPTION OF FLEXIBLE POLYMERS IN SMALL PORES

Pacelli Zitha

*Delft University of Technology, Faculty of Applied Earth Sciences, Mijnbouwstraat 120, 2628 RX Delft, The Netherlands*

We present experiments and the theory of the adsorption of flexible polymers under flow in disordered permeable materials. We focus on the case where the average chain end-to-end distance ( $R$ ) and the pore diameter ( $D$ ) are of the same order of magnitude (small pores). Two regimes can be distinguished according to whether the effective elongation gradient is low or large.

(1) Below a critical elongation gradient ( $\epsilon_c$ ) and at dilute conditions ( $C \ll C^*$ ) the chains have a statistical coil conformation with radius of gyration  $R_0$ . Their adsorption lead to the formation of layers with an hydrodynamic thickness  $\epsilon_H$  comparable  $R_0$  (layer adsorption). The resulting flow resistance is constant and the concentration profile along the core is uniform. The behavior in the semi-dilute regime ( $C > C^*$ ) is not completely clear.

(2) Above  $\epsilon_c$  the chains can be adsorbed in such a way that they form bridges over the pore constrictions (bridging adsorption). We derive the pore fractional coverage  $c_f$  as a function of an effective bridging-adsorption probability  $G$ . We obtain two situation depending on the relative intensity of local hydrodynamic forces. In the *weak flow* limit

$$c_f = 1 - (1 - Gt)^{1/2}$$

while in the *strong flow* limit

$$c_f = \frac{Gt / 2}{1 + Gt / 2}$$

Using a statistical up-scaling procedure, we derive the macroscopic flow resistance as a function of time and the corresponding concentration profile. The latter is shown to be non-uniform.

### 551.E3 THEORETICAL MODELS OF THE MASS TRANSFER AND SORPTION IN HETEROGENEOUS MEDIA

P. P. Zolotarev

*Institute of Physical Chemistry of Russian Academy of Sciences*

This report discusses the known phenomenological models of diffusion mass transfer and sorption in microheterogeneous nonporous and porous materials, containing the dispersion of inclusions (in the thermodynamic and kinetic senses) with a characteristic size  $l \ll L$ , where  $L$  is the dimension of the solid.

One-channel and two-channel models of double sorption with Henry and Langmuir isotherms are considered. The known solutions of the equations of these models are analyzed, including the solution of the so-called "inverse" problem on the determination of the parameters of the models from experimental data. The effect of the parameters of the above models on the shape of kinetic curves is studied using both exact and approximate solutions.

In order to illustrate the application of bidisperse models with the unbound and bound dispersed phases, their use is considered for analyzing the experiments on transient diffusion and sorption of the vapors of low molecular substances in two-phase polymeric materials (block-copolymers), and on the permeability of water vapor through porous polymeric films (diaphragms).

### 552.E4 EXCHANGE KINETICS OF POLY(ETHYLENE OXIDE) ADSORBED ON A SILICA SURFACE STUDIED BY EPR

A. Arif, H. Hommel, A.P. Legrand

*Laboratoire de Physique Quantique, URA 1428 CNRS, ESPCI,  
10 rue Vauquelin, 75231 Paris Cedex 05, France*

Polymers at Interfaces are interesting in applications such as chromatography in the laboratories or for paints and adhesion in industry and have therefore been widely studied. A particularly striking result has been obtained for polymers physically adsorbed on a solid: it seems practically impossible to wash out this polymer with the pure solvent, however it is possible to replace it with new chains of higher molecular weight.

In this work poly(ethylene oxide) of molecular weight 4000 terminally labelled with a nitroxide free radical is firstly physically adsorbed on amorphous silica, then a solution of poly(ethylene oxide) 10000 in cyclohexane is gently passed through the sample whilst the intensity of the Electron Paramagnetic Resonance is continuously recorded.

This intensity decreases regularly as the PEO 4000 is progressively removed. The linear variation suggests a convection/diffusion mechanism controlling the exchange.

### 553.E4 TRANSITION OF A STATISTICAL COPOLYMER ANCHORED AT THE AIR/WATER INTERFACE

Heiko Ahrens<sup>1</sup>, Klaus Lowack<sup>2</sup>, Christiane A. Helm<sup>3</sup>

<sup>1</sup>*Institut für Physikalische Chemie, Johannes Gutenberg - Universität, 55099 Mainz,*

<sup>2</sup>*Universität Potsdam, c/o MPI für Kolloid - und Grenzflächenforschung, 12489 Berlin,*

<sup>3</sup>*Fachrichtung Kristallographie, Universität des Saarlandes, 66041 Saarbrücken, Germany*

At the air/water interface a monolayer of random poly(methacrylate) copolymer with a hydrophobic and a hydrophilic substituent exhibits a transition from the fluid to a frozen state, which can be induced by lateral compression. By simplified FRAP-experiments (Fluorescence Recovery After Photobleaching) the reversibility of the freezing melting transition can be demonstrated. In the frozen phase amphiphilic guest molecules mixed with the random copolymer are immobile, which is demonstrated for biofunctional guest



molecules. The phase transition could be clearly observed with rheological experiments, in the fluid phase the increase of the viscosity by 3.5 decades could be described with the free area model. With small angle X-ray reflection, the electron density profile of the monolayer is investigated. Various hydrophobic substituents are tried. On compression, the electron density profile thickens (from about 1.5 nm to 2.5 nm) and the contrast improves, yet no obvious structural change can be correlated to the dynamic transition. This behaviour suggests a percolation transition.

#### **554.E4 THE NATURE OF NONPOLAR PHASE INFLUENCE ON ADSORPTION LAYERS PROPERTIES AT THE DROPLET'S INTERFASE INFLUOROCARBON AQUEOUS EMULSIONS AND FLOCCULATION**

**E.A. Amelina<sup>1</sup>, A.E. Chalykh<sup>2</sup>, E.E. Kumachova<sup>3</sup>, E.D. Shchukin<sup>1</sup>**

<sup>1</sup>*Moscow State University, Chemistry Department, Moscow, 119899, Russia.*

<sup>2</sup>*Institute of Physical Chemistry, Russian Academy of Sciences, Leninsky prospect, 31, Moscow, 117915, Russia.*

<sup>3</sup>*Toronto University, Chemistry Department, 80, Toronto, Ontario, Canada.*

TEM has been used in studying: (1) structure of the interfacial adsorption layers (IAL) of Proxanol 268 (block-copolymer of ethylene and propylene oxides, M.m.13000) at the perfluorodekalin (PFD) and perfluorotributylamine (PFTBA) droplets surface, and structure parameters of IAL estimation; (2) structure of the aqueous Proxanol solutions; (3) structure of emulsions flocculated with the excess of emulsifier (Proxanol). By the forque disk method, rheological behaviour of IAL has been studied at the interfaces between Proxanol aqueous solutions and PFD and PFTBA. A principal difference in the IAL structure has been observed: it is monoglobular, with the average globule size of 90 nm at the PFD droplets, - but more dense, and homogenous (noglobular), about 30 nm thick for PFTBA: in this last case, IAL reveals higher mechanical characteristics and stabilizing action against coalescence. Structure of IAL at PFD identical to the structure of the morphological inhomogeneity areas in Proxanol solution. This allows to suppose a nonspecific - for PFD, and specific - for PFTBA effect of the interface nature on the phase separation in the water/Proxanol system. PFD floccules are loose with globular bridges between droplets; on the contrary, PFTBA floccules are dense, their structure is compact, without bridges. Comparision of these observations with the structure of IAL and the morphological inhomogeneity areas in the water/Proxanol system witnesses different flocculation mechanisms in these emulsions.

#### **555.E4 PROPAGATION OF PHOTOINDUCED SURFACE PRESSURE PERTURBATION ALONG A MIXED BENZOSPIROPYRAN - OCTADECANOL MONOLAYER**

**K. Balashev<sup>1</sup>, I. Panaiotov<sup>1</sup>, J.E. Proust<sup>2</sup>**

<sup>1</sup>*Biophysical Chemistry Laboratory, University of Sofia, J. Bourchier str.1, 1126 Sofia, Bulgaria*

<sup>2</sup>*Pharmacie Galénique et Biophysique Pharmaceutique, Faculté de Pharmacie, 16 Bd Daviers, 49100 Angers, France*

The state and the elastic dilatational properties of a mixed spiropyran (with attached hydrocarbon chain) - octadecanol (1:5, mol/mol) spread monolayer were studied. A localized photochemical excitation was used to generate dilatational motion along the elastic monolayer. The surface pressure variations at various distances from the photoexcited region were measured. The experimental results are in quantitative agreement with a theoretical model taking into account the rheological properties of the interface and the liquid substrate as well as the rate constant for the photochemical process.

**556.E4****SURFACE MODIFICATION OF HYDROPHOBIC  
POLY(VINYLIDENE FLUORIDE) POROUS MEMBRANES****G rard Bauduin, Bernard Boutevin, and Alexandra Malinowa***Laboratoire de Chimie Appliqu e, Ecole Nationale Sup rieure de Chimie de Montpellier,  
rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France*

Porous hydrophobic poly(vinylidene fluoride) (PVDF) commercial (TECHSEP, Reference IRIS 3065 CGA 754) microfiltration membranes are modified by grafting of a hydrophilic monomer onto them in order to increase their permeability to water and aqueous solutions.

The average pore size of dry membranes is 0,22  $\mu\text{m}$  and they present a very low permeability to water. AMPSA (acrylamido propane sulfonic acid) is used as the hydrophilic monomer. It is reacted in aqueous solution under nitrogen, after electron beam activation of the membrane in air. The amount of grafted AMPSA is determined by weighing.

Three obtained membranes, with different grafting rates, are analyzed by contact angle measurements with pure water, FT-IR spectroscopy and scanning electron microscopy (SEM). The experimental results show that AMPSA is actually grafted on the membrane surface. The increase of the surface hydrophilicity causes a corresponding increase of the permeability of water through the whole membrane.

Some further studies by X-ray photoelectron spectroscopy (XPS) and attenuated total reflexion (ATR) FT-IR analysis are now in progress and will be presented at the Conference.

**557.E4****POLYELECTROLYTES AT HYDROPHILIC AND HYDROPHOBIC  
INTERFACES - A COMPARISON BETWEEN SILICA AND LATEX****D. Bauer, A. Fuchs, R. Rehmet, E. Killmann***Lehrstuhl f r Makromolekulare Stoffe, Institut f r Technische Chemie,  
Technische Universit t M nchen, Germany*

In addition to our paper about the adsorption of polyelectrolytes on silica-suspensions and the influences on the flocculation behavior we propose a comparison between hydrophilic silica and hydrophobic polystyrene-latex colloidal particles.

Poly(diallyl-dimethyl-ammonium-chloride) (PDADMAC) of different molecular weight and copolymers of DADMAC and N-methyl-N-vinyl-acetamide (NMVA) of different charge density are used again.

- On silica as well as on latex the adsorption isotherms are of the high affinity type.
- The charge density of the polystyrene-latex is much higher than that of silica. At low ionic strength this leads to higher adsorbed amounts in the plateau on latex than on silica due to charge compensation.
- The adsorbed amounts on both substrates show a strong increase with the ionic strength of the suspension.
- Because of the higher charge density latex has a greater train fraction at high salt concentration. This leads to lower adsorbed amounts in the plateau.
- At very high ionic strength a dependence on molar mass is observed at both substrates.
- Contrary to silica - where the adsorbed amounts rise with increasing pH - there is no influence of the pH-value on the adsorption on polystyrene-latex.
- At low coverage of the latex and silica particles flocculation occurs when the surface charge is screened enough either by small ions or by adsorbed macroions. At full coverage the stability of the suspensions depends on the thickness of the adsorbed layer, influenced by the salt concentration in the suspension, the charge density and the molar mass of the polyelectrolytes.

## 558.E4 POLYELECTROLYTE ADSORPTION AND STABILIZATION OF SILICA-SUSPENSIONS

D. Bauer, E. Killmann

*Lehrstuhl für Makromolekulare Stoffe, Institut für Technische Chemie,  
Technische Universität München, Germany*

Polymer adsorption is a very effective tool for controlling the stability of colloidal suspensions. We have investigated the influences of pH and salt concentration on the adsorption of linear polyelectrolytes on colloidal silica. Further we varied the molecular weight and charge density of the macroions. As polymers we used poly(diallyl-dimethyl-ammonium-chloride) (PDADMAC) and copolymers of DADMAC and N-methyl-N-vinyl-acetamide (NMVA).

The adsorption isotherms are of the high affinity type. The adsorbed amounts in the plateau rise with increasing salt concentration of the suspensions. At low ionic strength the polyelectrolytes show a flat conformation on the surface because of the repulsive interaction of the charges in the polyelectrolyte chain. The adsorbed amounts are dominated by charge compensation. With rising salt concentration the macroion-charges are screened by the low molecular salt ions. This leads to the formation of loops and tails and thus to higher adsorbed amounts. At high ionic strength the high molar mass polyelectrolytes show larger adsorbed amounts than polymers with low molar mass because of forming longer loops and tails.

With increasing pH of the solution the charge density of the silica particles becomes higher. In order to reach charge compensation the adsorbed amounts of the polyelectrolytes increase.

Stabilization and flocculation was investigated by photon-correlation-spectroscopy as a function of polyelectrolyte concentration, ionic strength and pH of the solution and molar mass and charge density of the polycations. At low ionic strength flocculation occurs just below full coverage of the surface where the surface charge is compensated by the charges of the adsorbed polyelectrolyte. At full coverage the surface charge is slightly over compensated by a surplus of the adsorbed macroions. This leads to a repulsive interaction between the particles, the suspension becomes stable.

At high ionic strength, where the particles show flocculation without any addition of polymer, the particles coagulate at low polyelectrolyte coverage. At full coverage the layer thickness of the adsorbed polymer determines whether the suspension becomes stable or not. Polyelectrolytes of high molar mass form long loops and tails and thus stabilize the particles sterically because of osmotic repulsion of the polymer chains. Macroions with low molar mass cannot prevent flocculation.

## 559.E4 MONOLAYERS AND SELF-ORGANIZED MULTILAYERS OF LIQUID CRYSTALLINE POLYORGANOSILOXANES AT THE WATER-AIR INTERFACE

S.I. Belousov<sup>1</sup>, E. Sautter<sup>2</sup>, N.N. Makarova<sup>3</sup>, W. Pechhold<sup>2</sup>, C. Knobler<sup>4</sup> and Y.K. Godovsky<sup>1</sup>

<sup>1</sup>*Karpov Institute of Physical Chemistry, Moscow, Russia*

<sup>2</sup>*University of Ulm, Germany*

<sup>3</sup>*Nesmeyanov Institute of Organo Element Compounds RAS, Moscow, Russia*

<sup>4</sup>*University of California, Los Angeles, USA*

Some novel linear and cycloliner (CLPOS) polyorganosiloxanes are able to form thermotropic 2D- or 1D-ordered polymeric mesophases which can be classified as columnar or platelike liquid crystals, respectively [1,2]. Recently, it has been established that CLPOS can be spread as Langmuir monolayers at surface densities of about 20 Å<sup>2</sup> per repeat unit [Si(R<sub>2</sub>)O] with the oxygens in the water surface and the side groups directed to the air [3-5]. Moreover, the majority of liquid crystalline CLPOS can form stable multilayers in response to compression: up to seven plateaus in pressure-area isotherms have been observed, the transitions between plateaus are characterized by sharp steps in pressure and are partly reversible. The plateaus occur at ratios of the area that are consistent with step wise layer growth from monolayer to bilayer, bilayer to trilayer, etc., continuing up to seven layers. The multistep behavior and formation of the multilayers is a direct consequence of the mesophase behavior of CLPOS (multilayer formation is not observed in CLPOS that do not form mesophases) and are closely related to the molecular structure of macromolecules (cycle size, side groups, flexible spacer, etc.). The multi-step isotherms have been interpreted by a model, in which the steps are treated as a result of sliding mechanism and mesophase

behavior, the mesophase being the stabilizing factor. The step-wise collapse has been studied in one of CLPOS by scanning force microscopy under topographic and frictional modes [6]. Topographic images show that the growth of the second layer begins with the nucleation of three-dimensional islands, which then appear to spread in the form of ribbons 0.5  $\mu\text{m}$  wide and 7.5  $\text{\AA}$  high. The number of ribbons increases as the extent of the second layer increases but the width of the ribbons remains constant. Subsequent layers show a more complicated morphology.

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## 560.E4

### BLACK FILMS OF LONG POLYMERS

J.J. Benattar<sup>1</sup>, F. Millet<sup>1</sup>, P. Perrin<sup>2</sup> and F. Lafuma<sup>2</sup>

<sup>1</sup>Service de Physique de l'État Condensé, DRECAM, CEA, F91191 Gif sur Yvette Cedex- France

<sup>2</sup>Laboratoire de Physico chimie macromoléculaire, ESPCI,  
10, rue Vauquelin F75 231 Paris Cedex 5 - France

We have shown using X-ray reflectivity experiments that the Newton black film (NBF) is a very well organized structure composed of two opposite walls of amphiphilic molecules without any liquid water between them; moreover such features are general even for very different chemical surfactants (ionic, non ionic and amphiphilic diblock copolyelectrolytes); thus the NBF is a very good model system for the direct study of interfacial phenomena such as interactions between surfactant bilayers. The aim of the present study is to provide a microscopic description of the air/water interface of specific hydrosoluble polymers, the hydrophobically modified poly(acrylic acid) which are used for the formation of emulsions. We present the first results obtained on black films, useful for the understanding of the stabilisation mechanisms of emulsions.

## 561.E4

### A STUDY USING A PARTICLE PROBE FORCE MICROSCOPE OF AN ADSORBED POLYMER LAYER

GJC Braithwaite and PF Luckham

Department of Chemical Engineering, Imperial College of Science Technology and Medicine, London, UK

In this presentation a description of the use of a Modified Atomic Force Microscope for the study of an adsorbed layer of polymer will be made. This extends the concept of a particle probe AFM to surface force measurement on an adsorbed bio-polymer layer. The paper will describe the change in the layer conformations with changing solution properties. In particular the pH and electrolyte concentrations will be adjusted, and the effect on the layer structure and thickness discussed. Highlighted will be the importance of these conditions, and the effect they have on the layer structure. Additionally, the critical nature of the adsorption conditions will be discussed.

## 562.E4 MOBILITY AND CONFORMATIONS OF POLY(ETHYLENE OXIDE) CHAINS GRAFTED ON SILICA UNDER A SHEAR FLOW OF SOLVENT

M. Chikhi, H. Hommel, A.P. Legrand

*Laboratoire de Physique Quantique, URA 1428 C.N.R.S., E.S.P.C.I.,  
10 rue Vauquelin, 75231 Paris Cedex 05, France*

The system polymer/silica surface have been studied very often to understand the behaviour of the chains. Such materials are indeed used in chromatography, tire industry, colloid stabilisation for example.

In this work we investigate with Electronic Paramagnetic Resonance of chains labelled with a nitroxide free radical the conformation of the polymers in a shear flow of solvent. The signal is very dependent on the microscopic Brownian motion of the label. The polymer is poly(ethylene oxide) of molecular weight 2000, the solid is amorphous silica and the solvent is cyclohexane. It is mainly the shear stress which is varied.

The EPR signal were simulated using the Kivelson theory and brought two types of information: statistical, with the fraction of segments in close contact with the surface, and dynamical, with the rotational correlation time of the motion of the label. Different regimes were observed depending also on the initial conditions and to the different treatments of the samples.

## 563.E4 INTERACTIONS BETWEEN TETHERED CHAINS AND SURFACTANTS

Terence Cosgrove<sup>1</sup>, Robin Wesley<sup>1</sup>, Laurie Thompson<sup>2</sup>, Stephen Armes<sup>3</sup> and Fiona Baines<sup>3</sup>

<sup>1</sup>*School of Chemistry, University of Bristol, UK.*

<sup>2</sup>*Unilever Research, Port Sunlight, The Wirral, Cheshire UK*

<sup>3</sup>*University of Sussex*

Tethered chains at the polymer-latex interface have been prepared by the incorporation of block copolymers into latex particles. The structure of these novel systems has been characterised by small-angle-neutron scattering and photon correlation spectroscopy. The effects of added surfactant have shown intriguing changes in the layers structure that are most pronounced at the critical micelle concentration.

Tethered chains are adsorbed polymers where the end segments are irreversibly attached to an interface. These systems can be prepared in several ways, but in this study they have been made by swelling a polymer latex and imbibing a block copolymer. One of the blocks is chosen to be compatible with the host latex and the other incompatible. In this instance two latex types [polystyrene: PS and poly(methyl methacrylate): PMMA] and two polymer types [PS-poly(ethylene oxide) and PMMA-poly(dimethylaminoethyl-methacrylate): PDMAEMA] have been used. The neutron data were obtained at the ISIS source in the UK and at NIST in the USA. Sodium dodecyl sulphate was used as the surfactant in both protonated and deuterated forms for contrast matching experiments.

The tethered chains formed brushes which were highly extended and were consistent with scaling predictions. For the unchanged system the polymer layer showed a slight contraction followed by a significant increase with increasing surfactant concentration. The PDMAEMA system showed rather richer behaviour as the layer structure depended strongly on pH and salt. With surfactant the layer followed a similar trend to the PEO data but with a rather more pronounced decrease followed by an expansion. In all cases, the maximum contraction was seen at the critical micelle concentration rather than at the critical aggregation concentration as might have been expected. These results echo findings with physically adsorbed layers where the decrease in thickness was attributed to a partial desorption of polymer.

## 564.E4 THE FEATURES OF GRAFT COPOLYMERS OF POLY(ACRYL AMIDE) TO DEXTRAN STATE IN WATER SOLUTIONS AND THEIR EFFECT ON THE ADSORPTION OF COPOLYMER AT SILICA SURFACE, ELECTROSURFACE PROPERTIES AND STABILITY OF SILICA SUSPENSIONS

Eremenko B.V., Malysheva M.L., Zeltonozskaya T.B

*Taras Shevchenko University, Vladimirskaya str. 64, 252017 Kiev, Ukraine*

Water-soluble graft copolymers of poly(akrylamide) to dextran (D-PAA) are effective regulators of stability of disperse systems. They belong to a new class of polymer compounds-intramolecular polycomplex (IMPC).

It was shown that a large size of graft copolymer macromolecule in solution combines with a rigid intramolecular structure, which is conditioned by system of H-bonds between the basic and grafted chains and between grafted PAA chains. It was shown that water is close to a theta-solvent for D-PAA. The increase of temperature from 298 to 308 K causes the conformational transition from IMPC to segregated state and the formation of polymolecular (D-PAA) micelles.

Adsorption of graft copolymers on the silica surface (aerosil) does not change the value of surface charge but causes the sharp decrease of absolute values of electrokinetic potential. The adsorption and electrokinetic potential values do not depend on the quantity of grafted PAA chains per macromolecule.

Macromolecules of graft copolymers were shown to formate thick adsorbed layers on silica surface. The comparison of "electrokinetic" thickness of adsorbed layers with macro-molecular sizes in solution testifies about a considerable deformation of IMPC while passing to the surface. This phenomenon is conditioned by concurrent interaction in polymer-colloid system which leads to preferential bounding of grafted PAA chains with silica surface.

Addition of alkali causes the distraction of IMPC and this leads to weakening of adsorptional interaction between copolymer and silica surface.

The formation of adsorbed copolymer layers causes the stabilization effect on aqueous suspensions of quartz. In acid solution (pH=2) suspensions are stable; 1:1 electrolyte does not coagulate these suspensions up to concentration equal 2500 mmol/l. Stabilization effect of copolymers is conditioned by sterical component of disjoining pressure and it becomes stronger with increasing of copolymer concentration and ionic power of solution.

At neutral pH addition of copolymer causes stabilization of only small particles which present in suspension, but the sensibilization effect takes place for the largest particles. The last is connected with the appearance of deep potential minimums on interaction energy curves.

In alkaline solutions copolymer shows polyelectrolyte properties. As a result the sterical component of disjoining pressure grows weak and electrostatic repulsion, connected with the charge of macromolecules, becomes stronger. This leads to the decrease of stabilization effect of copolymer on quartz suspensions.

## 565.E4 POWER-LAW EXPONENT IN THE CENTRAL REGION OF A POLYMER LAYER ADSORBED FROM DILUTE SOLUTION: COMPARISON BETWEEN SCALING AND SCF RESULTS

G.J. Fleer

*Department of Physical and Colloid Chemistry, Agricultural University,  
Dreijenplein 6, 6703 HB, Wageningen, The Netherlands*

De Gennes predicted the self-similar structure of adsorbed layers with a volume fraction profile that scales as  $\phi(z) \propto z^{-\alpha}$  in the semi-dilute (central) region of the adsorption profile of homopolymers. This power-law behaviour is recovered in mean-field SCF calculations. In this case the exponent is  $\alpha=2$  in good solvents provided  $D \ll z \ll d$ , where  $D$  is the proximal length and  $d$  the distal length. We use a ground-state approximation (GSA) to derive expressions for the two length,  $D$  and  $d$ , and show that in the central region the profile is in good approximation given by  $\phi = 1/3(z + D)^{-2} \exp(-(z + D)^2 / 3d^2)$ . Unless the chains are extremely long the condition  $D \ll z \ll d$  is difficult to obtain and corrections on the exponent are necessary. For most chain lengths in the experimental range, the central region is quite narrow. It is shown that for high adsorption energies (small  $D$ )  $\alpha \approx 2 + 2d^{-1}$  in leading order, where  $d \approx R_g (\ln(1/\phi^b))^{-1/2}$ , with  $R_g$  the radius of

gyration and  $\phi^b$  the bulk solution concentration. For weak adsorption the proximal length  $D$  is larger, which leads to a smaller exponent  $\alpha$ . The  $d^{-1}$  correction is in excellent agreement with numerical self-consistent-field calculations.

In poor solvents  $\phi = 1/2(z + D)^{-1} \exp(-2(z + D)^2 / 3d^2)$  and  $\alpha \approx 1 + 4d^{-1}$  in the strong adsorption limit, which implies a larger correction in this case. Our analysis suggests that in a polymer adsorption profile with excluded-volume correlations (where  $\alpha = 4/3$ ) non-universal aspects would also be present if the chain length is finite.

## 566.E4

### NEW POLYSACCHARIDES AS EMULSIFIERS

N. Garti, K. Meiri and A. Aserin

*Casali Inst. of Applied Chemistry, The Hebrew Univ. of Jerusalem, 91904 Jerusalem, Israel*

Fenugreek gum is extracted from the *Trigonella Foenum-graecum* seeds and evaluated for its surface activity. This unique galactomannan has a mannose backbone grafted with galactose units at an average ratio of 1:1 (mannose:galactose). The objective of this research is to investigate the emulsification properties of fenugreek gum as a food emulsifier. The purified fenugreek gum was found to reduce surface tension ( $\gamma_0 = 42$  mN/m vs. 50 mN/m for Guar gum) and its interfacial activity was better than of other galactomannans ( $\gamma_i = 20$  mN/m vs. 27 mN/m for LBG). This enhanced activity led to the formation of oil-in-water emulsion with small droplets (2-5  $\mu$ ) and long term stability. The fenugreek gum was found to adsorb to the oil interfaces (birefringence) forming interfacial film.

This research further explores the role of the protein (11 wt% in the crude gum, 3 wt% in purified gum and 1.2 wt% in bipurified gum) to the gum's adsorption capacity and its emulsification ability. It was found that bipurified gum with lower protein content imparts better stability to the oil water emulsion than that composed of high protein.

We also attempted to enzymatically hydrolyze the high-molecular weight gum (over  $10^6$  daltons) to smaller fractions with MW of 100,000 to 20,000. We expect to find that the small fractions have improved flexibility and better adsorption capacity.

## 567.E4 FRACTIONATION OF POLYELECTROLYTES DURING ADSORPTION

Geffroy C.<sup>1</sup>, Persello J.<sup>1</sup>, Foissy F.<sup>1</sup>, Cabane B.<sup>2</sup>, Tournilhac F.<sup>3</sup>

<sup>1</sup>*Laboratoire d'Electrochimie et des Systèmes Microdispersés, Besançon, France*

<sup>2</sup>*CEN Saclay, Chimie Moléculaire, Gif sur Yvette, France*

<sup>3</sup>*Rhône-Poulenc Recherche, Aubervilliers, France*

Adsorption of polymers onto mineral surfaces has been modelled in the case of oxides and the influence of molecular weight has been quite well understood. In that case, it is supposed that the adsorbed fraction will be that of higher molecular weight. Concerning charged macromolecules, in the presence of high salt concentrations, their behaviour was found to be that of neutral bodies.

However, fractionation has been early noticed by Cafe and Robb. In most cases, the adsorbed fraction can be assessed by making the difference between the initial and residual weight distribution. To our knowledge however, no report on a direct determination has been published. We have studied the adsorption of sodium polyacrylate onto calcium carbonate and we have directly determined the adsorbed fraction by a Size Exclusion Chromatography method. We have focused on the electrostatic interactions between charged bodies by an original experiment. For that purpose, in various conditions, the solid has been separated after contact with the polymer and has been fully dissolved, the bare adsorbed macromolecules being further analysed.

It has been found that polymers of low molecular weight do preferentially adsorb what supports the assumption that the adsorption is kinetically controlled. A minimal molecular mass allowing adsorption has also been observed what has been correlated to a minimum segmental adsorption energy.

The influence of the ionic strength, and valency of the added cation has also been investigated. We directly observe the displacement of the distribution's peak toward the higher molecular weights in the

presence of salt. This phenomenon lead credence to the existence of a potential energy barrier brought in by the first adsorbed macromolecules.

This study allows a better understanding of the adsorption mechanism of polyelectrolytes onto mineral surfaces. Moreover, there is strong evidence of the influence of the kinetic factor, which combined to the electrostatic one, can lead to a stable situation primor to the thermodynamic state of equilibrium (what predicts the adsorption of high molecular fractions).

## 568.E4

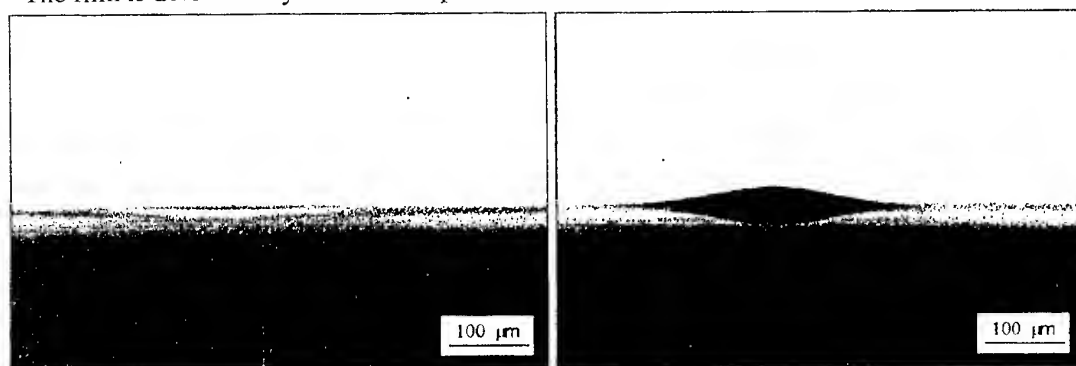
### MONOLAYERS OF A SOLVENT FREE POLYMER BRUSH: FREELY SUSPENDED CROSSLINKED FILMS

Werner A. Goedel

Max-Planck Institut für Kolloid- & Grenzflächenforschung,  
Haus 9.9, Rudower Chaussee 5, 12489 Berlin, Germany

Hydrophobic polymers with low glass transition temperature (polyisoprenes) and a single head group (sulfonate) bearing photoreactive side groups (anthracene) have been synthesised and characterised as insoluble monolayers on a water surface. The isotherms are similar to the parent polymers without anthracene side groups and the films can be transferred to solid substrates via the Langmuir-Blodgett technique with a transfer ratio of 0.85. The films on solid substrates as well as on the water surface can be crosslinked via irradiation with UV-light. Films crosslinked on the water surface can be transferred to substrates with holes in the millimeter range. The films span the openings and most likely are rubber elastic.

Suspended crosslinked membrane spanning a 0.3 mm hole seen from the side.  
The film is deformed by a small overpressure from below.



Heger & Goedel, *Progr. Coll & Polymer Sci.*, submitted 1996

## 569.E4

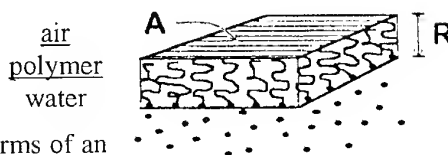
### MONOLAYERS OF A SOLVENT FREE POLYMER BRUSH: THERMODYNAMICS AT THE AIR/WATER INTERFACE

Werner A. Goedel

Max-Planck Institut für Kolloid- & Grenzflächenforschung,  
Haus 9.9, Rudower Chaussee 5, 12489 Berlin, Germany

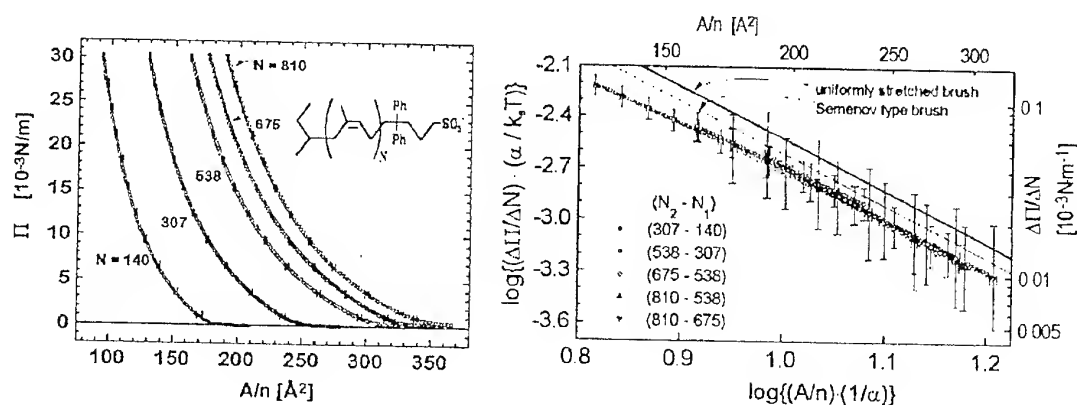
Hydrophobic polymers with low glass transition temperature and a single head group have been synthesised and characterised as insoluble monolayers on a water surface. A single ionic head group is sufficient to make these hydrophobic polymers surface active and isotherms of an expanded type have been recorded.

These isotherms can be described quantitatively using a theory based on constant density of the hydrophobic region, Gaussian chain statistics and affine deformation: At a fixed area per head group, the





surface pressure is proportional to the length of the hydrophobic tail. The slope of this relation is proportional to the third power of the area per head group. Chains shorter than 300 repeat units systematically deviate from the theory. (Heger & Goedel, *Macromolecules*, 1996, 29 (27)).



## 570.E4

### ENZYMATIC HYDROLYSIS OF POLY (D,L - LACTIDE) SPREAD MONOLAYERS BY CUTINASE

Tz. Ivanova<sup>1</sup>, I. Panaiotov<sup>1</sup>, F. Boury<sup>2</sup>, J.E. Proust<sup>2</sup>, R. Verger<sup>3</sup>

<sup>1</sup>Biophysical Chemistry Laboratory, University of Sofia, J. Bourchier str 1., 1126 Sofia, Bulgaria

<sup>2</sup>Pharmacie Galénique et Biophysique Pharmaceutique, Faculté de Pharmacie,  
16 Bd Daviers, 49100 Angers, France

<sup>3</sup>ERS 26 «Lypolyse enzymatique» du Centre National de la Recherche Scientifique,  
B.P.71, F-13402 Marseille Cedex 9, France

The enzymatic hydrolysis of a model poly (D,L - lactide) by cutinase was studied by using a barostat surface balance. A theoretical approach based on the adaptation of the Michaelis-Menten scheme at the interface and a process of random fragmentation of the macromolecules was developed. The role of the interfacial organisation of the reaction products was discussed. Hydrolysis rate constant values and the specific activity were estimated and compared with those obtained for the hydrolysis of lipid monolayers.

The process of fragmentation of the interfacial polymer structures was visualised by using AFM imaging.

### 571.E4 RHEOLOGICAL CHARACTERISTICS OF INTERFACIAL ADSORPTION LAYERS OF INTERPOLYMER ASSOCIATES (POLYSTYRENE AND COPOLYMER OF STYRENE WITH METHACRYLIC ACID/GELATIN FORMED ON THE LIQUID INTERFACES OF O-XYLENE/ WATER

V.N. Izmailova<sup>1</sup>, I.A. Gritzikova<sup>2</sup>, Habibolla. Baharvand<sup>1</sup>, A.A. Kapustina<sup>2</sup>,  
P.V. Nuss<sup>3</sup>, L.G. Izmailov<sup>1</sup>, E.V. Martynova<sup>2</sup>

<sup>1</sup>Moscow State University, Faculty of Chemistry, Moscow, Russia

<sup>2</sup>Moscow State Academy of Fine Chemical Technology, Moscow, Russia

<sup>3</sup>Institute of Eye Diseases, Russian Academy of Medical Sciences, Moscow, Russia

The properties of mixed interfacial adsorption layers (LAL) which contain some surfactant-components water- and oil-soluble are essential at consideration of biological systems in number of technological processes.

The measurements of thermodynamic (interfacial tension) and rheological (by using the method of constant deformation velocity) characteristics were carried out in conditions of constant ( $T=20^\circ\text{C}$ ) temperature on the interface between water solution and o-xylene solution.

Rheological curves of flow for IAL of polystyrene in o-xylene, of styrene copolymer with methacrylic acid in o-xylene on the water interface and water solution of gelatin on the o-xylene interface

and their interpolymer complexes (polysterene and copolymer of styrene with methacrylic acid and with gelatin) formed on the o-xylene/water interface are characterized by elastic and viscosity parameters.

Interpolymer complexes which were formed on the liquid interface observe synergetic effect of rheological parameters. This is responsible for appearance of additional electrostatic interactions of polyelectrolytes (with opposite charges) on the interfaces.

## 572.E4 MICELLIZATION OF DIBLOCK COPOLYMERS AS A FUNCTION OF THE BLOCK ASYMMETRY.

D.Izzo<sup>1</sup> and C.M.Marques<sup>2</sup>

<sup>1</sup>*Instituto de Fisica, Universidade Federal do Rio de Janeiro, CP 68528, 21945-970, Rio de Janeiro, RJ, Brazil*

<sup>2</sup>*Institut Charles Sadron, 6 rue Boussingault, 67093, Strasbourg Cedex, France.*

We consider a solution of diblock copolymers in a selective solvent. Blocks "A" and "B" have polymerisation indices  $N_A$  and  $N_B$  respectively; monomers in blocks "A" are incompatible with the solvent. We take into account all regimes of asymmetry  $N_A/N_B$  and obtain a sequence of phases. In the  $N_A/N_B \ll 1$  region, we have direct structures in which dense cores are surrounded by well swollen coronas forming a dilute system; in the other limit,  $N_A/N_B \gg 1$ , semi-concentrated phases set in, where swollen cores are immersed in a dense matrix. We follow a description in terms of classical approximation to a self consistent field method; nevertheless this description is shown not to be valid everywhere, and in these regions we adopt the Alexander-de Gennes approximation. An order-of magnitude estimate for asymmetry values where the transitions are expected to occur is also obtained. These are confirmed by the full phase diagram obtained by solving numerically the analytical equations.

## 573.E4 DEPRESSION OF HYDROPHOBIC MINERALS BY NON-IONIC POLYMERS - THE ROLE OF ADSORBED POLYMER LAYER STRUCTURE

Paul Jenkins and John Ralston

*Ian Wark Research Institute, University of South Australia, Adelaide, SA 5095, Australia*

The adsorption properties of two classes of non-ionic polymers onto hydrophobic talc particles was studied. The natural polysaccharide, guar, and triblock poly(ethyleneoxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) copolymers, produced by ICI under the trade name Synperonic, were the polymers chosen for investigation. Adsorption isotherms for both guar and the PEO-PPO-PEO copolymers were of high affinity and capacity (ca.  $1 \text{ mg m}^{-2}$ ) in various different electrolyte solutions. The Langmuir model was applied to calculate the free energy of adsorption  $\Delta G_{\text{ads}}$  of the respective polymers onto the talc surface.  $\Delta G_{\text{ads}}$  for both guar and the Synperonics was found to be strongly negative. This was ascribed to a strong hydrophobic interaction that exists between the talc surface and the polymers.

Guar is often used to depress talc during the flotation process. Microflotation tests were performed to contrast the depressant performance of PEO-PPO-PEO with that of guar. Studies showed that the depression of talc by guar was dependent upon electrolyte type and strength. Specifically, the rate of flotation of talc was always reduced when guar was present, whilst the maximum recovery of talc was much lower in low ionic strength electrolytes and those containing multivalent ions. The PEO-PPO-PEO copolymers proved to be totally ineffective talc depressants. In fact, the maximum recovery of talc obtained was not reduced with the addition of the Synperonic copolymers, whilst the rate of talc flotation was significantly enhanced particularly when multivalent ions were present in the electrolyte solution.

The disparity in talc depression performance of the two strongly adsorbing polymers studied is attributed to differences in the conformation of the adsorbed polymer at the talc-aqueous interface. Electrophoretic mobility and rheological measurements were used to estimate the adsorbed layer thickness and the effective surface area occupied by a polymer chain was calculated from adsorption isotherm data. This information was subsequently used to calculate the average volume fraction of polymer in the adsorbed layer. The volume fraction of guar was estimated to be some 4 times greater than that of the PEO-PPO-PEO copolymer. Both are in good agreement with neutron scattering studies and theoretical segment density

profiles calculated by Scheutjens-Fleer theory. These results tend to support the notion that a polymer will act as an effective talc depressant if the adsorbed layer is relatively dense, since such a layer is more likely to be able to resist the ingress of a bubble towards the mineral surface.

## 574.E4 STRUCTURE, MODIFICATION OF POLYETHYLENETEREPHTALATE TRACK ETCHED MEMBRANES AND THEIR ADSORPTION PROPERTIES IN WATER

**T.D. Khokhlova<sup>1</sup>, B.V. Mchedlishvili<sup>2</sup>**

<sup>1</sup>*Laboratory of Adsorption and Chromatography, Chemical Department, M.V. Lomonosov,  
Moscow State University, 119899 Moscow*

<sup>2</sup>*Laboratory of Nuclear filters, Institute of Crystallography of Russian Academy of Sciences,  
117333 Moscow, Russia*

Ultrafiltration membranes made from polyethyleneterephthalate irradiated on cyclotron U-400 in Flerovs Laboratory of Nuclear Reactions in Dubna are investigated. Their structure is estimated using electron microscopy, mercury intrusion, capillary condensation and nitrogen adsorption at 77 °K. The pore volumes, specific surfaces and average pore diameters are about 0,02-0,07 cm<sup>3</sup>/g, 2-8 m<sup>2</sup>/g and 30-60 nm, correspondingly. Adsorption in water of proteins and dyes take place generally owing to hydrophobic and with surface carboxyl groups interactions. Adsorption of basic dye Rhodamine C correlated with specific surface of membranes and so may be used for its determination. Adsorption of proteins at pH 2-10 is investigated. Adsorption maximum is placed at pH some lower isoelectric point pI of protein. The largest adsorption to 7mg/m<sup>2</sup> is observed for  $\gamma$ -globulin. There is adsorption of neutral ( $\gamma$ -globulin, hemoglobin) and basic proteins ( lysozyme, cytochrome C, ribonuclease A,  $\alpha$ -chymotrypsin) at any pH investigated and their adsorption is greater than one of acid proteins (albumin and ferritin). There is not adsorption of acid proteins at pH higher in 3-5 units. Probably negative charges on the protein globules and on the surface of membranes ( its pI about 2-3) prevent from adsorption because of electrostatic repulsion. Track etched membranes are modified with 3-aminopropylthriethoxysilane in aqueous solution. Adsorption of acid dye Alisarinsaphirol SE is used to estimate covering completeness and its stability in water. Adsorption of basic proteins on modified membranes in comparison with unmodified ones significantly decreased, of neutral proteins slightly decreased and of acid proteins slightly increased. These effects may be explained by presence of aminopropyl groups on modified membrane surface.

## 575.E4 ASSOCIATIVE AND SEGREGATIVE PHASE SEPARATIONS IN POLYMER-PARTICLE-SOLVENT SYSTEMS

**Andrey A. Litmanovich, Yuriy Ye. Kuzovlev and Yelena V. Polyakova**

*Moscow State Automobile and Road Technical University 64, Leningradsky Prosp.,  
Moscow 125829, Russia*

Several approaches are used to describe peculiarities of phase separation in systems including macromolecules, colloidal particles, and solvent, namely:

- (i) separation due to incompatibility (segregative process);
- (ii) separation due to insoluble, stoichiometrical polymer-particle complex (PPC) formation (associative);
- (iii) separation due to non-stoichiometrical PPC formation, which solubility is a function of composition (also associative).

The systems are known to form gels at high concentrations of both macrocomponents; (colloid) solutions, at low concentrations; and two macroscopic phases, at intermediate concentrations. The tasks are:

- (1) description of components distribution between two macroscopic phases;
- (2) description of concentration border "solution - two phases";
- (3) description of concentration border "two phases - gel".

Task (1) may be clarified using combination of approaches (i)+(ii). It is shown that a sharp transition from regime (i) to regime (ii) should take place on varying external conditions (pH, temperature, etc) affecting polymer-particle interaction parameter.

Tasks (2) and (3) demand spinodal equation to describe phase instability of the system.

It is shown that approach (i) gives an appropriate description of the border "solution - two phases" (spinodal surface transsection at fixed temperature in coordinates 'volume fraction of polymer-volume fraction of particles' gives a hyperbolic curve). On the contrary, in the case of approach (iii), the transsection looks like two hyperbolic curves conjugated in the regions where concentration of one component is very high, and that of another, rather small. It means that approach (iii) permits to describe both named concentration borders.

Correspondence of theoretical picture to experimental data is discussed.

The authors are grateful to Russian Foundation of Fundamental Researches for financial support (Grant No 95-03-09214).

## 576.E4 COLLOIDAL FORCES INDUCED BY ADSORBED POLYMERS

O. Mondain-Monval, J. Philip, F. Leal Calderon, J. Bibette

*Centre de Recherche Paul Pascal - CNRS, Av. A. Schweitzer, 33600 Pessac, France*

Using a recently developed technique (Leal Calderon et al., Phys. Rev. Lett. 1994), we report direct measurements of the force distance profiles between emulsion droplets in polymer solutions of various nature.

The forces between droplets covered by neutral (polyvinyl alcohol PVA) or charged (polyacrylic acid PAA) polymers are probed. In PVA solution, the force-distance profiles are measured as function of the polymer concentration, molecular weight and solvent quality. The measured repulsive forces are exponentially decaying and the range is shown to scale roughly as the polymer gyration radius. Such exponential force-distance scaling is also observed in PAA solutions of high ionic strength and seems to be independent of the nature of the adsorbed polymer. In polyelectrolyte solutions, we probe the evolution from a regime where the forces are due to double layer repulsion (at high pH and low ionic strength), to the regime where the repulsion is mainly steric (at high ionic strength). Between these limit situations, we observe the appearance of an instability in the force profile that leads to the irreversible aggregation of the droplets. All our results are compared to recent theories on polymer induced forces.

## 577.E4 A QUARTZ CRYSTAL MICROBALANCE STUDY OF PROTEIN ADSORPTION AT GOLD AND HYDROPHOBIC GOLD SURFACES

Brent S. Murray and Lauren Cros

*Food Colloids Group, The Procter Department of Food Science,  
The University of Leeds, Leeds LS6 9JT, UK*

The kinetics of adsorption of pure milk proteins  $\beta$ -lactoglobulin and  $\beta$ -casein, and a commercial cationic gelatin, have been studied at the gold-water and hydrophobic gold-water interfaces via a quartz crystal microbalance (QCM). The resonant frequency change,  $\Delta f$ , of the QCM with adsorbed protein is higher than that predicted by the theoretical Sauerbrey equation. These frequency shifts are due not only to adsorbed protein amount, but also to changes in protein interactions with water. As such the QCM measurements have not provided accurate information about the adsorbed protein amount, but possibly very useful information about hydrodynamic layer thickness, i.e., changes in the structure of the adsorbed films. At neutral pH, both  $\beta$ -lactoglobulin and  $\beta$ -casein form a protein monolayer at the interface that can be divided into a protein-rich inner layer close to the interface and a more diffuse hydrophilic outer layer extending into the bulk aqueous phase.

Changes in  $\Delta f$  on addition of octaethylene glycol n-dodecyl ether ( $C_{12}E_8$ ) at surfactant-to-protein molar ratio of 16 suggest displacement of protein from the interface, except for  $\beta$ -lactoglobulin adsorbed on gold. A surfactant-protein complex is formed and can be later partially or totally removed from the interface by diluting with solvent.

Gelatin adsorption onto hydrophobic gold induces a very high  $\Delta f$ , indicative of interfacial gel formation with a large water entrapment. Addition of  $\beta$ -lactoglobulin to a 24-hour-old gelatin film induces a

further large increase in  $\Delta f$  consistent with the known capacity of these two proteins to form an electrostatic complex at hydrophobic interfaces.

## 578.E4

### INTERFACES IN THE SYSTEM POLYDIMETHYLSILOXANE AND FUMED SILICA. QUANTUM-CHEMICAL MODELLING

E. Nikitina<sup>1</sup>, V. Khavryutchenko<sup>2</sup>, E. Sheka<sup>3</sup>, H. Barthel<sup>4</sup> and J. Weis<sup>4</sup>

<sup>1</sup>*Institute of Applied Mechanics, Russian Academy of Sciences, Leninsky prospekt, 32A, Moscow, 117334 Russia*

<sup>2</sup>*Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Kiev, 251028 Ukraine and Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, 141980 Russia*

<sup>3</sup>*Russian Peoples' Friendship University, General Physics Department, ul. Ordjonikidze 3, Moscow, 117302 Russia*

<sup>4</sup>*Wacker-Chemie GmbH, Werk Burghausen, D-84480 Burghausen, Germany*

The presented study is devoted to a microscopic approach to the adsorption interactions between polydimethylsiloxanes (PDMS) polymers and hydroxylated fumed silica surfaces. The analysis of this interfacial system is of high technical interest, aiming at a better understanding of the atom scale mechanisms which control the reinforcement of silicone elastomers by fumed silica. A modified semiempirical AM1 method [1] together with MNDO/H and PM3 techniques was used for this purpose. A preliminary study on models like  $(\text{H}_3\text{SiO})_3\text{SiOH}$  demonstrated the limitations of the competence of molecular silanol centers. A four-layered amorphous silica cluster with 48  $\text{SiO}_{4/2}$  units bearing isolated surface hydroxyl groups provided a more realistic model of the surface of hydrophilic fumed silica particles. A linear and a cyclic oligomer, containing five silicon atoms each, dodecamethylpentasiloxane (Si5) and decamethylcyclopentasiloxane (D5), were chosen as appropriate models of the PDMS polymer. The total-energy-minimization procedure to obtain equilibrated cluster structures for 1:1 adsorption complexes has been performed. The adsorption mechanism is discussed in terms of changes in the dipole moments, changes in the molecular structures and changes in the charge distributions of the adsorbed oligomers, owing to the interactions with the silica surface. Additionally, shortest atom-atom distances and Wiberg coefficients at the interface of the complexes are presented. The modelling results did not reveal any detectable H-bonds. However, the modelling results demonstrate that adsorption has a marked impact on the dipole moment of the adsorbed oligomer. Adsorption also affects the internal structure of the oligomer molecules. Both impacts, changes of the dipole moment and intermolecular distortions, are more pronounced for the cyclic oligomer D5 than for the linear oligomer Si5. The adsorption energies of the PDMS oligomers on the hydroxylated silica surface are in good agreement with recent experimental data [2]. It could be demonstrated that the adsorption energies correlate well with the calculated shortest atom-atom distances. Obviously, the PDMS oligomer adsorption is governed by nonspecific dispersive interactions, mainly. Structures and topology of the active sites of adsorption on the hydroxylated silica surface are discussed.

1. E.F. Sheka, V.D. Khavryutchenko, E.A. Nikitina, *Phys. Low-Dim. Struct.*, 1995, 1, 1

2. A. Khalfi, E. Papirer, H. Balard, H. Barthel, M. Heinemann, *J. Coll. Interf. Sci.*, 1996, in press

## 579.E4

### THICKNESS TRANSITIONS OF BLACK FOAM FILMS FORMED FROM DMPC/DPPE-PEG2000 DISPERSIONS

A. Nikolova<sup>1</sup> and M.N. Jones<sup>2</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*School of Biological Sciences, University of Manchester, Manchester M13 9PT, UK*

Foam films formed from aqueous dispersions of dimyristoylphosphatidylcholine, DMPC, and dipalmitoylphosphatidylethanolamine with covalently bound poly- (ethylene glycol) of molecular weight 2000, DPPE-PEG2000, were studied by the thin liquid film microinterferometric technique of Scheludko and Exerowa in the temperature range 14-36°C. The dispersions were prepared by solvating the amphiphiles in chloroform/methanol solvent, evaporation of the solvent and hydration in aqueous solution of electrolyte.

The mean size of the vesicles was within the range 50-200 nm. The kinetics of amphiphile adsorption at the air/(aqueous dispersion) interface was followed by surface tension measurements in order to choose appropriate conditions for the formation of the foam films. These measurements show that the surface coverage for the dispersions containing only one amphiphile (DPPE-PEG2000) is very slow in the temperature range studied and does not reach equilibrium values within reasonable time intervals. The dispersions containing DMPC/DPPE-PEG2000 mixture showed much faster destruction of the vesicles and coverage of the air/(aqueous dispersion) interface at temperatures above 24°C, the temperature of the chain-melting phase transition of the main lipid component (DMPC). The foam films were equilibrated at 36°C before measurement of the film thickness. The dependence of the equilibrium thickness of the foam films on the electrolyte concentration was measured for 1 and 9 mol % DPPE-PEG2000 at 28°C. It is shown that the long-range molecular interactions in these films are nearly identical with the ones in the foam films stabilised with DMPC. At the physiological electrolyte concentration (about 0.14 mol.dm<sup>-3</sup> NaCl) two types of foam bilayers were formed. A temperature - composition dependence of the bilayer thickness was measured. The transition between the two types of bilayers occurs at about 3-4 mol % DPPE-PEG2000 within the temperature range studied. The data for the foam bilayer thickness and the comparison with the phase diagrams of the PC/DPPE-PEG dispersions show that the foam bilayers studied exist in two phase states characterised by different conformation (brush or mushroom) of the grafted polymer.

## 580.E4

### CONFORMATIONAL TRANSFORMATIONS OF POLYMETHACRYLIC ACID MACROMOLECULES UNDER THEIR ADSORPTION FROM AQUEOUS SOLUTIONS ON THE CHARGED SURFACE

D.M. Nykypanchuk, Z.M. Yaremko, L.B. Fedushyns'ka

*L'viv State University named after Ivan Franko, Kyryla i Mefodija, 6, L'viv, 290005, Ukraine*

Polyelectrolytes are widely used to control aggregation and sedimentation stability of colloid systems. Their stabilization effect can be explained in terms of adsorption layer formation on particle's surface. The adsorbed layer changes a balance of long-range surface forces, which responsible for aggregation stability of the colloid systems. The stabilization effect of the adsorbed macromolecules is determined by adsorbed layer structure and in particular by the conformation of the polyelectrolyte macromolecules on the charged surface. The hydrogen of the hydroxide ions are potential determinant for a surface of oxides, thus macromolecules in the adsorption layer on the surface are located in medium with the pH gradient. The results of research on properties of PMAA (polymethacrylic acid) solutions independence on neutralization degree of the macromolecules are presented in the paper. Three samples of PMAA of different molecular weight have been investigated. The relative viscosity, the conductivity, the diffusion coefficient and the pH of the medium as a function of alkali amount added to the polyacid solution have been studied. The conformational transformations of PMAA depending on the neutralization degree have been analyzed and corresponding models have been developed. The obtained results were compared with ellipsometry measurements of the thickness of an adsorbed polymethacrylic acid layer on the silicon dioxide surface.

## 581.E4

### PREPARATION OF WATER REDISPERSIBLE POLYMER POWDERS: SPRAY DRYING OF ANIONIC POLYMER DISPERSIONS IN PRESENCE OF CATIONIC PROTECTIVE COLLOIDS

Joachim Pakusch, Sabine Vogt, Walter Mächtle, Joachim Roser

*BASF AG, D-67056 Ludwigshafen/Germany*

The poster presents some of our recent work aimed at understanding a new preparation process for water redispersible polymer powders<sup>1</sup>. This process comprises the use of cationic protective colloids in spray drying anionic polymer dispersions. The cationic protective colloids have high glass transition temperatures ( $T_g$ ) while the dispersion polymers typically have a  $T_g$  below room temperature.

No coagulation occurs during the mixing of the cationic protective colloid and the anionic polymer dispersion. It was possible to prepare completely water-redispersible polymer powders by spray drying these protected polymer dispersions at air temperatures well above 100°C without irreversible film formation.

The reason for the unexpected stability of the mixture is the charge inversion of the polymer particles. These are initially charged anionically and become cationically charged by rapid addition of the dispersion to the protective colloid solution under stirring <sup>2,3</sup>. This is confirmed by measurement of the electrophoretic mobility in dependence of pH and protective colloid content.

The point of electrophoretic neutrality is reached at a protective colloid content of about 1.5 weight % (based on solids content of the polymer dispersion). This value is also obtained by quantitative determination of the water-soluble part of the pure dispersion and its mixtures with the protective colloid by analytical ultracentrifuge measurements. This is actually the saturation concentration for surface adsorption. At concentrations higher than 1.5%, excess amount of protective colloid will stay in the serum of the protected polymer dispersion; nevertheless it contributes to the stability of the latex.

A mixture of a n-butyl acrylate/styrene copolymer dispersion and 15 weight-% (based on solids content) of a N-vinyl pyrrolidone/quaternarized N-vinyl imidazole copolymer has been dried to a completely water-redispersible polymer powder.

The described redispersible polymer powders are especially useful for two main applications:

- paints or non-hydraulic plasters, where the powder is applied as the only binder,
- modification of hydraulic (i.e. cementitious) systems, where the addition of powder leads to a highly flexible hardened material.

1. BASF AG, EP to be laid open (Prior. 28.10.1995)

2. Polysar Financial Services S.A., EP 305 039 (Prior. 15.7.1987)

3. The Dow Chemical Co., US 3 205 187 (Prior. 22.9.1960)

## 582.E4 POLYANILINE-POLYCHLOROPRENE SURFACE COMPOSITES

Magali Silveira Pinho<sup>1</sup>, Marianna Gorelova<sup>2</sup>, Márcia Dezotti<sup>2</sup> and Bluma Guenther Soares<sup>2</sup>

<sup>1</sup>*Instituto de Pesquisas da Marinha, Rio de Janeiro, R J, Brazil*

<sup>2</sup>*Institute de Macromoléculas, Universidade Federal do Rio de Janeiro,  
P. O. Box 68525, Rio de Janeiro, R J, Brazil*

The interest created by the discovery of high conductivity in polyacetylene (PA) upon doping with the original oxidative dopants iodine (I<sub>2</sub>) and arsenic pentafluoride (AsF<sub>5</sub>) in the late 1970's stimulated increasing activity in the study of polymers with conjugated backbones such as polyaniline, polypyrrole, poly(p-phenylene sulfide), polythiophene, etc. The aniline family of polymers has been the subject of recent interest because of their high electrical conductivity, environmental stability, solution processability and interesting redox properties associated with the chain nitrogens. For this reason, these polymers are considered as highly promising new materials for electronic devices, electrochromic displays, electrical applications, polymer batteries, polymer modified electrodes, and functional membranes.

Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization of aniline in acidic aqueous medium and is unique among conducting polymers in that its electrical properties can be reversibly controlled both by charge-transfer doping and by protonation. Polychloroprene (CR) is an elastomeric material with great resistance to chemical attack by acids, suitable for blending with this conductive polymer. In this study, electrically conductive polyaniline-polychloroprene (PANI-CR) composites have been prepared by "*in situ*" polymerization. This is a simple, technically feasible process using the chemical oxidative polymerization of aniline at the interface of the elastomeric material. The formation of PANI on the surface of CR is based on a interfacial mechanism by a physical liquid-solid interaction.

The formation of PANI-CR surface composite has been studied by a surface sensitive technique X-Ray Photoelectron Spectroscopy (XPS).

Analysis of N1s core lines in PANI-HCl (ES) spectrum allowed the investigation of different surface functional groups of N in doping samples. The balance of benzenoid amine and positively charged nitrogens, with bindings energies at about 399.2 and 401.0 eV, respectively, was studied.

The degree of doping was obtained through the ratio surface elemental stoichiometries Cl/N. It was determined by XPS as 0.50 for pure PANI and as 0.44 for the "*in situ*" polymerization, which was in good agreement with theoretical values.

Good adhesion properties coupled with desirable environmental stability suggests applications in stealth technology, camouflage and similar military applications.

The authors would like to thank the financial support from CNPq, CAPES,CEPG-UFRJ, PADCT-FINEP and IPqM.

## 583.E4

### THE ESTIMATION OF SURFACE ENERGY OF POLY- $\alpha$ -CYANOACRYLATES BY QUANTUM CHEMICAL DATA

L.M. Pritykin, A.N. Lyubchenko, O.B. Selyutin, V.I. Bolshakov  
Pridneprovsk State Academy of Construction and Architecture P.O. Box 1449,  
Dnepropetrovsk 320127, Ukraine

The exposure of the connection between the surface energy of condensed phases ( $\sigma$ ) with the chemical nature of objects has the principal meaning for different branches of modern chemistry and physics because the named energy plays the key role in the description of any process proceeding on surfaces. Such an attempts were usually limited by the microscopic approximation using various *molecular* characteristics for solid or liquid objects as function's of  $\sigma$  argument. It's evident that the accounting of precision details of molecular *electron* bonding must be taken as the basis for defined dependences. However, the required manner for the surface energy estimation on the basis of quantum chemical data, as we informed, hasn't been developed consequently. We investigated this problem applying to the adhesion known as one of the most important surface phenomena because  $\sigma$  value is the first adhesion-sensitive parameter of any low- and high-molecular compounds. Poly- $\alpha$ -cyanoacrylates (PCA) were naturally chosen as the objects for calculation because of their most progressive adhesive universal character and their surface energy was preliminary securely calculated by refractometric and viscosimetric characteristics of respective monomers. Such a manner seems to be most grounded, because only monomers in contrast to polymers can be correctly quantitatively characterized on the submolecular level. We made such an estimation taking into account the thermodynamical nature and dimension of  $\sigma$  value with the next quantum chemical characteristics of PCA ( $X_q$ ) embracing all the energy of monomer electron bonding, - potential energy of electrones in molecule ( $E_m^e$ ) and their sum for each  $i$ -atom ( $\sum_i E_a^e$ ), repulsion energy between skeletones ( $E_n^{rep}$ ), atomization energy ( $E_m$ ) and enthalpy of molecule ( $H_m^0$ ). The named characteristics were calculated in approximation of well-known scheme NDDO by AM1 method with preliminary total geometry optimization according the Polak-Rieber algorithm. All dependences between the  $\sigma$  and  $X_q$  values can be described only by the equation of first  $\sigma = a + bX_q$  (1) or second  $\sigma = a + bX_q + cX_q^2$  (2) order. It's important that Eq.1 securely and adequately describes the investigated dependence. That's why  $c \ll b$  not occasionally, hence we can ignore  $c(X_q)$  term in Eq.2 (see Table).

Table

Coefficients of Functions and Correlations and Standard Deviations for the Desired Functions were  
Calculated of  $\sigma(X_q)$  1st (Numerator) and 2nd (Denominator) Orders for P- $n$ -alkCA

$X_q$	$a$	$b$	$c$	$r$	$\Delta_{rel}, \%$
$-E_m^e$	380 36,3	$0.977 \cdot 10^{-5}$ $0.259 \cdot 10^{-4}$	$-0.340 \cdot 10^{-10}$	0.997 0.979	0.8-3.1 2.6-8.1
$E_n^{rep}$	38.2 36.8	$0.111 \cdot 10^{-4}$ $0.281 \cdot 10^{-4}$	$-0.452 \cdot 10^{-10}$	0.996 0.997	0.9-3.6 0.8-3.5
$-\sum_i E_a^e$	36.2 31.6	$0.888 \cdot 10^{-4}$ $0.292 \cdot 10^{-3}$	$0.220 \cdot 10^{-8}$	0.994 0.990	0.2-1.7 1.8-3.8
$-E_m$	37.8 36.2	$0.104 \cdot 10^{-2}$ $0.249 \cdot 10^{-2}$	$0.304 \cdot 10^{-6}$	1.000 0.990	0-0.6 1.8-3.8
$-H_m^0$	37.7 35.9	0.046 0.113	$0.593 \cdot 10^{-3}$	0.987 0.993	0.2-11.5 0-5.6



**584.E4****STRUCTURE, MORPHOLOGY, AND DEGRADATION  
OF POLY(- $\alpha$ -HYDROXY ACIDS) MICROSPHERES IN RELATION WITH HYDROLYSIS  
OF SPREAD MONOLAYERS****J.E. Proust<sup>1</sup>, I. Panaiotov<sup>2</sup>, F. Boury, Tz. Ivanova<sup>2</sup>, R. Verger and J.P. Benoît**<sup>1</sup>*Pharmacie Galénique et Biophysique Pharmaceutique, Faculté de Pharmacie,  
16 Bd.Daviers, 49100 Angers, France.*<sup>2</sup>*Biophysical Chemistry Laboratory, University of Sofia, J.Bourchier str. 1., 1126 Sofia, Bulgaria.*<sup>3</sup>*ERS 26 "lipolyse enzymatique" CNRS, B.P.71 13402 Marseilles France.*

Microparticulate controlled release systems, prepared from polyester such as poly(D,L-Lactide-co-glycolide) (PLGA) are often used as drug delivery device. In vivo the polyester matrix undergoes a chemical degradation (hydrolysis process) producing a totally bioresorbable product. The influence of various degradation factors as pH of the medium, the presence of hydrolytic enzymes, the molecular weight and polydispersity was intensively investigated in vitro and in vivo.

We have prepared various microspheres of PLGA containing bovine serum albumin (BSA) as model protein. The study of the surface properties and of the superficial structures performed by wettability and by Atomic Force Microscopy (AFM) measurements have shown the influences of the polyester composition and of the formulation process. AFM measurements reveal too the modification with time of the superficial structure observed on microspheres. These measurements performed *in situ* on microspheres are compared with results obtained for Langmuir-Blodgett films prepared from the same polyester spread monolayers. In particular, using this monolayer model, we have studied the hydrolysis degradation of polyesters.

Acidic, basic or enzymatic hydrolysis of polyester spread monolayers was studied by using a barostat surface balance. A theoretical approach based on a process of random fragmentation of the macromolecules and a solubilization of the small oligomers was developed. The role of the interfacial organization of the monolayers characterized by isotherm analysis and AFM measurements on Langmuir-Blodgett films was discussed.

The study of the hydrolysis by acidic or basic interaction allowed us to determine the rate and the mechanism in the beginning of the reaction. The rate constant which is a function of the surface pressure, increases with the increasing of the number of the ester bonds per unit area able to be hydrolyzed and is maximum for the pressure corresponding to the inflection point on the isotherms. In the later stages of the hydrolysis, we observe an inhibition process due to the accumulation of insoluble charged products.

The study of enzymatic hydrolysis of a model poly(D,L-Lactide)monolayer by cutinase based on the adaptation of the Michaelis-Menten scheme at the interface and a process of random fragmentation of the polymer molecules allowed us to determine the global rate constant of the enzymatic reaction. In this case, contrarily to the basic or acidic reactions, the course of the reaction is faster in the later stages of the hydrolysis because the preferential binding of the cutinase on the negatively charged substrate obtained by accumulation of insoluble products formed at the interface.

**585.E4****A STUDY OF THE SURFACE PROPERTIES OF SILICA WITH BONDED  
BROMOPROPYLPOLYSILOXANE LAYERS****T.M. Roshchina, V.Ya. Davydov, M.S. Timoshic, A.A. Mandrugiu***Moscow State University, Chemistry Department,  
Laboratory of Adsorption and Chromatography, Moscow, Russia*

The methods of gas chromatography (GC) and of adsorption in static conditions were used for investigation of surface properties of initial silica and modified silicas containing different amount of chemically bonded bromopropyl groups. Adsorption isotherms of nitrogen were measured at 77 K. The thermodynamic characteristics of adsorption (TCA), including Henry constants and differential initial heats of adsorption, of saturated and aromatic hydrocarbons, oxygen-, nitrogen- and chlorine-containing compounds were determined at low surface coverage by GC. TCA depended on the concentration of bromopropyl groups on the silica surface. Modification of the silica with the polymer film of bromopropyl groups eliminated the tailing of peaks of compounds capable of specific interactions and considerably

reduced the TCA of such molecules. Silica surface is thus strongly deactivated upon grafting of bromopropylpolysiloxane layers. The values of TCA of n-alkanes are higher on bromosilica than on initial support. This increase could be associated with the "solvation" of the adsorbed molecules by the grafting chains. It was shown that the magnitude of specific interactions on bromosilica increased from ethers to esters and further to alcohols. The study revealed that the adsorption properties of modified silica varied with species of grafted chains. We observed an increase of TCA of molecules capable of donor-acceptor interaction on bromosilica in comparison with silica containing bonded polymer film of aminopropyl groups. This fact may be explained by the electrophilic properties of bromopropyl radicals. The results obtained may be used for the estimation of the range of application of bromosilica both as an adsorbent in GC and as a product for posterior modification.

## 586.E4 A NEW METHOD FOR DIRECT FORCE MEASUREMENTS OF BULK POLYMERS USING THE MASIF - SURFACE FORCES APPARATUS

F.-J. Schmitt<sup>1</sup>, T. Ederth<sup>2</sup>, P. Weidenhammer<sup>1</sup>, P. Claesson<sup>2</sup> and H.-J. Jacobasch<sup>1</sup>

<sup>1</sup>*Institute of Polymer Research, PO Box 120411, D-01005 Dresden, Germany*

<sup>2</sup>*Royal Institute of Technology and Institute of Surface Science, PO Box 5607, Stockholm, Sweden*

A new method for direct force and adhesion measurements on bulk polymer samples was developed. Polymer samples were prepared by forming droplets of a polymer melt. These droplets maintain their shape and smoothness during cooling and were directly mounted into the MASIF surface forces apparatus. This novel apparatus uses a solid state force sensor (bimorph), which acts as the force measuring spring as well as the force sensor device. It allows measurements with opaque samples or solutions, but does not give absolute distance measurements or the surface morphology. We measured the interaction of two polystyrene samples in air, water and in the presence of a surfactant solution. In air and water, the contact between the two polystyrene bodies leads to cohesive failure and damage. In the presence of the surfactant, the polystyrene surfaces are covered with a thin adsorbed layer of the surfactant, which reduces the adhesion drastically. This measurements show the feasibility of direct force measurements with the MASIF surface forces apparatus for bulk polymer samples and may open a new field in surface characterization.

## 587.E4 SCALING BEHAVIOR OF BLOCK COPOLYMERS AT THE LIQUID/AIR INTERFACE

R. Sedev and D. Exerowa

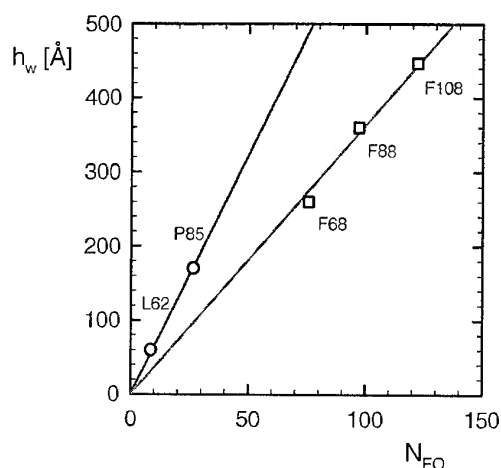
*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

Amphiphilic block copolymers adsorb at the liquid/air interface as do common surfactants: the hydrophobic block tries to escape from the aqueous solution while the hydrophilic remains inside. If the surface concentration exceeds a certain limit the hydrophilic chains are crowded at the interface and consequently stretched, i.e. they form a brush layer. The scaling behavior of the brush thickness,  $L$ , is [Alexander (1977), de Gennes (1981)]:

$$L \cong aN\sigma^{1/3}$$

where  $a$  is the monomer size,  $N$  the degree of polymerization and  $\sigma$  the dimensionless surface density ( $\sigma = a^2/d^2$ ,  $d$  - average lateral distance between grafted chains).

If two liquid/air interfaces are brought together a thin foam film is created. This can be easily done in the Scheludko-Exerowa cell. Electrostatic interactions are suppressed by the addition of 0.1 M NaCl. The two adsorption layers are softly compressed - the disjoining pressure is  $10^2$ - $10^3$  dyn/cm<sup>2</sup>, and therefore the measured film thickness,  $h_w$ , should be a good approximation of the double brush thickness,  $2L$ .



The equilibrium film thickness,  $h_w$ , for several  $\text{EO}_{\text{NEO}}\text{-PO}_{\text{NPO}}\text{-EO}_{\text{NEO}}$  copolymers (commonly known as Pluronics, Synperonics or Poloxamers) is plotted in Fig.1.

The linear scaling with  $N$  is followed quite strictly (lines are drawn through the origin). However the data segregate into two distinct categories and the pertinent parameter is the asymmetry ratio,  $\beta = N_{\text{EO}}^{3/5}/N_{\text{PO}}^{1/2}$ , listed in the table below. More asymmetric copolymers exhibit lower increment. Similar results have been obtained with the surface force apparatus [Hair et al. (1991)]. Common nonionic surfactants exhibit similar behavior.

Name	M	$N_{\text{PO}}$	$N_{\text{EO}}$	$\beta$
L62	2,500	30	8.5	0.7
P85	4,600	39	26	1.1
F68	8,400	30	75	2.4
F88	10,800	39	97	2.5
F108	14,000	56	122	2.4

If the relationship  $\sigma \propto \beta^{-m}$  is introduced into the above equation it appears that  $m = 5/4$  or  $9/5$ .

## 588.E4 ADSORPTION OF CATIONIC POLYELECTROLYTES ON CHARGE-REGULATING SURFACES: EXPERIMENTAL STUDY AND THEORETICAL MODELLING

Victor Shubin<sup>1</sup> and Per Linse<sup>2</sup>

<sup>1</sup>St. Petersburg University, St. Petersburg, Russia

<sup>2</sup>Lund University, Lund, Sweden

Adsorption of two cationic polyelectrolytes with low and medium linear charge density onto mono-disperse silica and carboxylfunctionalized polystyrene latex, respectively, was studied via polyelectrolyte and potentiometric titration. Surface charge density ( $\sigma_0$ ) of the bare substrates and that in the presence of adsorbed polyelectrolyte layers, as well as the adsorbed amount ( $\Gamma$ ) were measured over a wide range of pH and KCl concentrations ( $c_s$ ). The experimental results allowed to estimate a number of important characteristics of the studied systems, including intrinsic equilibrium constants of dissociation of surface functional groups and of counterion binding.

An extension of the self-consistent-field (SCF) lattice theory of polyelectrolyte adsorption, which takes into account electrochemical equilibria at the interface (charge regulation), is proposed. The choice of major parameters of the model was based on characteristics of the real systems and the number of free fitting parameters was reduced to a minimum.

Theoretical calculations of surface charge density, adsorbed amount, and degree of surface charge compensation by polyelectrolytes as a function of pH and electrolyte concentration were conducted and the results were compared with corresponding experimental data. The extended SCF model describes well (on quantitative level) the surface charge density of the substrates both in the presence and in the absence of adsorbed polyelectrolyte. The theory is also successful in prediction of the main features of the surface charge overcompensation upon polyelectrolyte adsorption under different electrolyte conditions (pH,  $c_s$ ). At the same time the adsorbed amount is predicted rather poorly.

We suggest that the discrepancies between the experiment and the theory are due to imperfections in theoretical description of interfacial conformation of macromolecules and/or to nonequilibrium aspects of polyelectrolyte adsorption, which can not be described by the present equilibrium theory.

## 589.E4 SURFACE TENSION OF POLYMER AQUEOUS SOLUTIONS: GRAFT COPOLYMERS VERSUS BLENDS

Cristiane X. Silva, Gleyciane S. Pereira and Elizabete F. Lucas

*Instituto de Macromoleculas Professora Eloisa Mano/UFRJ, 68525, Z.C. 21945-970, Rio de Janeiro, Brazil*

Copolymers made up of different chemical sequences act as surfactants. Polyacrylamide (PAAm) and poly(ethylene oxide) (PEO) are water soluble and poly(propylene oxide) (PPO) is not water soluble. In this work, graft copolymers of poly(acrylamide-g-ethylene oxide) (PAAm-g-PEO) and poly(acrylamide-g-propylene oxide) (PAAm-g-PPO) were synthesized and their compositions were analysed by nuclear magnetic resonance ( $^{13}\text{C}$ -NMR). Aqueous solutions of the pure homopolymers (PAAm and PEO), graft copolymers (PAAm-g-PEO and PAAm-g-PPO) and blends of PAAm/PEO and PAAm/PPO were prepared. The surface tension measurements of the polymer aqueous solutions were carried out in a digital tensiometer Krüss, K-10, using the De Nouy ring, at 30°C. The surface tension of water is about 73 dyn/cm. The PAAm and PEO homopolymers do not reduce the surface tension markedly. The graft copolymers of PAAm-g-PEO showed a behavior between the pure homopolymers and it was not observed graft chain content dependence on the surface tension. On the other hand, blends of PAAm/PEO could reduce the aqueous solutions surface tension to lower values than the PAAm-g-PEO and the lowest values were achieved at around 50/50 blend composition. Graft copolymers of PAAm-g-PPO showed higher reduction of surface tension values than PAAm-g-PEO due to its structure which is made up of hydrophilic and hydrophobic segments. Besides, the surface tension values changed as a function of graft size and content. By comparing PAAm-g-PPO and PAAm/PPO aqueous solutions it was observed that, at the same composition, the results were very similar. It implies that surface tension measurements could become a simple and practical method to determine these graft copolymers composition.

The authors would like to thank the financial support from CEPG/UFRJ, CNPq, CAPES and FINEP.

## 590.E4 ASSEMBLY OF POLYELECTROLYTE MULTILAYER FILMS ON THE SURFACES OF COLLOID PARTICLES

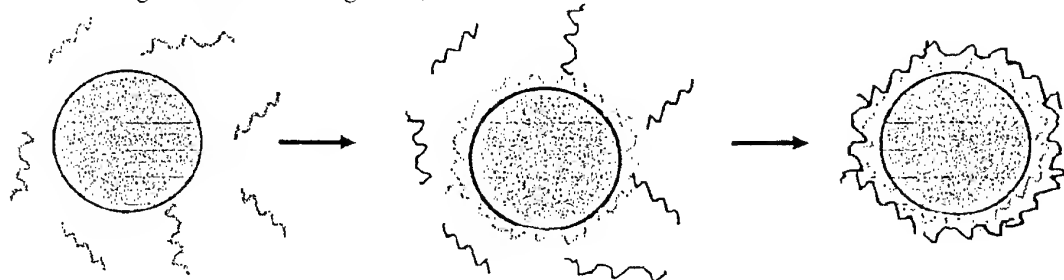
C.B. Sukhorukov<sup>2</sup>, H. Zastrow<sup>1</sup>, H. Lichtenfeld<sup>1</sup>, E. Donath<sup>1</sup>, H. Möhwald<sup>1</sup>

<sup>1</sup>*Max Planck Institute for Colloids and Interfaces, Berlin, Germany,*

<sup>2</sup>*Institute of Crystallography, Rus.Acad.Sci., Moscow, Russia*

The recently developed protocol of consecutive adsorption of oppositely charged polyelectrolytes onto flat surfaces has been investigated for colloid particles by depositing polyelectrolyte films. Two sets of polystyrene latex particles have been studied: (i) 640 nm in diameter, prepared in this laboratory, stabilised by sulphate groups, and (ii) 100 nm, ex SPECHT GmbH, stabilised by NaAOT. These were used to investigate the conditions of consecutive polyelectrolyte multilayer growth. The polycation (grey on the figure) was added to negatively (black) charged particles. Three centrifugation steps followed each deposition step, in order to remove the unbound polyelectrolyte before the next oppositely charged polyelectrolyte was added, to prevent interpolyelectrolyte complex formation. For the polycations we used poly(diallyldimethylammonium chloride) (PDADMAC) and poly(allylamine hydrochloride) (PAH). The polyanions were poly(sodium styrene sulfonate) (PSS) and DNA. A well-pronounced net charge, of opposite sign, was observed after each polyelectrolyte adsorption step from zeta-potential measurements using the Zetasizer microelectrophoresis equipment (ex MALVERN instruments). In contrast to the previously used flat surfaces, the first polycation layer was found to be unstable with time. We attributed this behavior to the penetrable nature of the polystyrene particle surface. However, addition of the second layer inhibited this process. The overcharging per surface area was investigated as a function of the polyelectrolyte concentration. The data are consistent with a mechanism of a gradual irreversible coverage up to complete saturation of the particle surface. The adsorption characteristics of the first layer, however, were different from the subsequent ones. This was again attributed to the softness (or roughness) of the naked particle surface. Electrophoretic fingerprints were taken to obtain information on the multilayer internal electrostatic and hydrodynamic properties. Next, multilayers were deposited without the centrifugation steps. This was achieved by adding polyelectrolyte at bulk concentrations close to, but still slightly below, saturating conditions. The idea was to avoid close particle-particle contact in the centrifugation pellet. Ultrasonication

and a subsequent filtration followed, in order to remove any particle aggregates that formed. An increase in the hydrodynamic particle size was demonstrated for up to 16 consecutively deposited polyelectrolyte layers using Photon Correlation Spectroscopy. Single Particle Scattering Photometry was also applied to measure the thickness of adsorbed layers and to estimate the degree of doublets, triplets etc. formed. The features, advantages and disadvantages of both of the protocols used are discussed. The possibility of depositing polyelectrolyte films on colloidal particles, rather than flat surfaces, allows for a broader variety of methods to be applied for the study of the principles of polyelectrolyte film assembly. In addition, these investigations should lead to the development of a new class of colloids whose surface properties, such as molecular composition, charge and surface roughness, can be controlled.

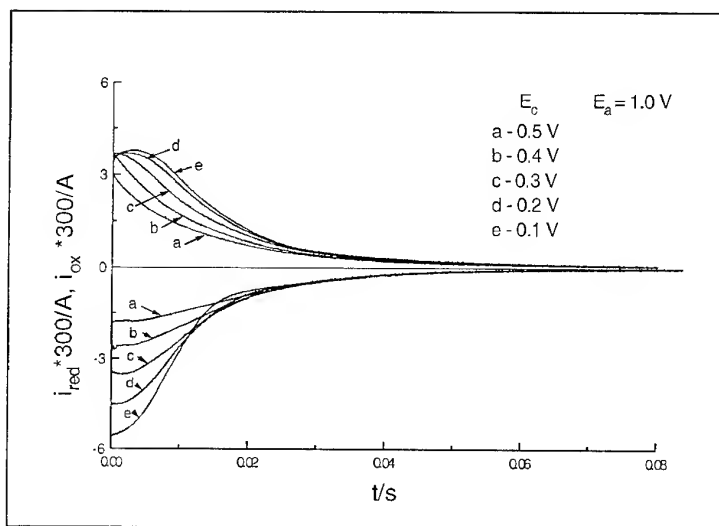


## 591.E4 STUDY OF THE REDOX BEHAVIOUR OF THIN POLYANILINE FILMS

Vessela Tsakova

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*

Thin polyaniline(PAN) films were electrochemically deposited on a platinum substrate using a specially designed pulse potentiostatic procedure[1,2]. PAN films thus obtained can be reduced and subsequently oxidized by applying constant cathodic  $E_c$  and respectively anodic  $E_a$  potentials. The corresponding reduction  $i_{red}$  and oxidation  $i_{ox}$  currents were measured in order to study the electrochemical redox behaviour of the polymer films.



As should be expected (see Figure) the reduction currents measured for different cathodic potentials are increasing with decreasing values of  $E_c$ . The oxidation currents however show a peculiar behaviour - instead of continuously increasing with decreasing  $E_c$ , a flattened maximum appears for  $E_c < 0.3$  V which is slightly influenced by further decrease of the cathodic potential. In fact the inhibition of the oxidation process is observed when the PAN films have been previously reduced to an insulating state and thus it should be related to the transition of the polymer structures from non-conducting to

conducting state.

According to Kalaji et al [3] the non-conducting/conducting transition in the polymer films can be considered as a phase transition process. The present study suggests an interpretation of the experimental oxidation transients by means of a theoretical model for instantaneous nucleation and two-dimensional growth.

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## 592.E4 A TOTAL INTERNAL REFLECTION FLUORESCENCE SPECTROMETER TO STUDY PROTEIN ADSORPTION AT OIL/WATER INTERFACES

M.J. Tupy, H.W. Blanch, and C.J. Radke

*Chemical Engineering Department, University of California, Berkeley, CA 94720 USA*

Adsorption of proteins at the oil/water interface is important in protein separation processes, enzymatic catalysis, and protein-stabilized emulsions. To obtain information on the molecular structure and dynamics of proteins at the oil/water interface, we have constructed a novel total internal reflection fluorescence spectrometer (TIRFS). Monochromatic, polarized light is focused through a prism onto the oil/water interface below the critical angle, producing an evanescent wave that excites fluorophores attached to or naturally occurring in the adsorbing proteins. An important aspect of the apparatus is that the adsorbing species arrive by one-dimensional diffusion from the bulk solution to the interface. A stagnant 10  $\mu\text{m}$  thick water layer is sandwiched between the oil/water interface and a porous polymeric membrane covering a flow channel. The flow channel allows us to introduce aqueous soluble, fluorescing surface active species of increasing or decreasing concentrations to the TIRFS and to follow the dynamics of sorption quantitatively. Further by using a monochromator, we measure the fluorescent spectrum of the adsorbed species to gain insight into the chemical environment of the fluorescent probe. Thus, our unique TIRFS design enables the kinetics of protein adsorption to be gauged, as well as provides assessment of adsorption reversibility and molecular conformation changes in a single, noninvasive experiment.

Studies to date have examined the adsorption of  $\beta$ -casein and ovalbumin at an oil/water interface. We find that protein accumulation at the interface is well described by a simple diffusion model with the known bulk diffusion coefficient. Additionally, experiments testing reversibility clearly confirm that a significant fraction of the adsorbed protein does not desorb over a period of many hours. Separate experiments using pendant-drop tensiometry and transmission electron microscopy of the protein films harvested from the interface show significant interfacial aggregation and network formation of the protein, indicative of a thick, gelatinous layer. Protein adsorption at the oil/water boundary appears to be a slow, irreversible denaturation process that eventually generates a gel-like interphase.

## 593.E4 MODELLING OF THE ADSORPTION OF POLYELECTROLYTES ON $\text{CaF}_2$

K.E. Wong Fong Sang, J.H. ter Horst, C.H. de Vreugd, R.M. Geertman,  
G.J. Witkamp, G.M. van Rosmalen

*Delft University of Technology, Laboratory for Process Equipment, Leeghwaterstraat 44,  
2628 CA, Delft, The Netherlands*

Additives are frequently applied to retard crystal growth either completely to prevent e.g. scaling or on specific crystal faces to obtain a product with a specific habit. In general, a large negative adsorption energy of the additive causes a high surface concentration, which hampers the crystal growth.

Calcium fluoride ( $\text{CaF}_2$ ) was chosen as a model compound to investigate the adsorption of the polyelectrolytes polyacrylate (PA) and polymaleate (PM) at different pH conditions because of its importance in the biomineralization.  $\text{CaF}_2$  has a cubic unit cell with the Fm-3m space group. Experimentally grown  $\text{CaF}_2$  crystals are bounded by the {100} or {110} faces. It was found that the surface concentration  $\Gamma$ , of the polyelectrolyte decreases with increasing pH, and that the polyelectrolytes decrease the growth rate of  $\text{CaF}_2$  crystals (figure 1).

The objective of this investigation was to find an explanation for the observed experimental results by using molecular modelling techniques. The adsorption energies were calculated using Cerius<sup>2</sup> software by combining molecular dynamics (MD) and molecular mechanics (MM). MD was used to cover a wide area of possible configurations after which the configurations with the lowest potential energies were minimised with aid of MM. In these calculations PA molecules with smaller molecular weights ( $M_w=650$ , number of monomers  $n=9$ ) were taken than those used experimentally ( $M_w=3700$ ,  $n=50$ ) to prevent extremely long calculation times.

The adsorption energy of PA is obtained by subtracting the energy of the minimised configuration in vacuum from that on the crystal surface. The energy calculations were performed for adsorption on the (100) (figure 2) and on the (110) surfaces. The results (figure 2) show the same qualitative trend as the experiments

(figure 1). It can therefore be concluded that molecular modelling can in principle be used as a predictive tool for polyelectrolyte adsorption on ionic crystals.

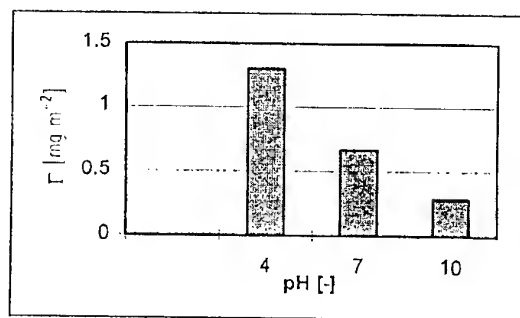


Figure 1: Surface concentration  $\Gamma$  of PA as function of pH,  $M_w=3700, n=50$ .

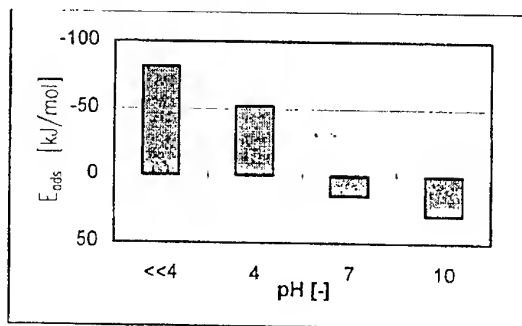


Figure 2: Adsorption energy  $E_{ads}$  per monomer of PA ( $n=9$ ) on the (100) surface as a function of pH.

## 594.E4

### HYDROPHOBIZED POLYCATIONS ON THE SURFACE OF NEGATIVELY CHARGED LIPOSOMES

Ekaterina G. Yaroslavova, Mikhail O. Ignatiev, Valery Ye. Koulkov,  
Alexander A. Yaroslavov and Viktor A. Kasaikin

*Faculty of Chemistry, Moscow State University, Leninskie Gory, Moscow 119899, Russia*

Interaction of synthetic polycations with cell and artificial lipid membranes has been studied for a long time. Less attention was paid to study of such interaction in the presence of a polyanion capable to form strong interpolyelectrolyte complex (IPEC) with polycation and thus, to influence adsorption of polycation onto the cell membrane. Hydrophobization of polycation molecule by either covalent attachment of side-chain fatty fragments, or complexation with negatively charged surfactants, seems to be a promising way to increase stability of polycation-membrane contact. To check the idea, we undertook a model study using (i) quaternized derivatives of poly(4-vinylpyridine), (ii) negatively charged liposomes, and (iii) polyacrylic acid (PAA).

The four polycations were used in the work. The first was poly(N-ethyl-4-vinylpyridinium bromide) (P2). The three others contained, together with ethyl groups, a small amount (about 4 mol.%) of heptyl, or dodecyl, or cetyl groups (P7, or P12, or P16, respectively). Small liquid liposomes were prepared from mixture of negatively charged diphosphatidylglycerol (cardiolipin, CL) and neutral phosphatidylcholine (PC) with the molar content of negatively charged CL head groups equal to 0.2.

It was found that addition of polycations to liposome suspension led to neutralization of the liposome surface charge and particle enlargement. All the polycations were completely adsorbed on the liposome surface, and about 90% of their quaternized units formed ionic contacts with negatively charged CL head groups. Importantly, the integrity of liposomes contacting the polycations, even containing rather long dodecyl and cetyl side-chain radicals, remained unchanged.

At the same time, the polycations interacted with liposomes in different ways. P2-liposome interaction was mainly of electrostatic nature. This polycation could be completely displaced from the liposomal membrane by addition of the excess of PAA that resulted in formation of negatively charged nonstoichiometric interpolyelectrolyte complex (IPEC). This process was accompanied by desegregation of large polycation-liposome complex particles down to the initial liposomes.

Modification of polymer chain by alkyl fragments resulted in additional stabilization of polycation-liposome complexes, probably due to incorporation of alkyl fragments into the hydrophobic part of liposomal membrane. Stabilization effect became stronger with increasing alkyl fragment length. It was found that PAA couldn't displace P16 from the liposome surface, but was able to interact with a part of positively charged P16 units thus yielding ternary polyanion-polycation-liposome complex.

It was found also that negatively charged PAA-P16 IPEC could interact with negatively charged liposomes as a whole. Therefore, complexation with a hydrophobized polycation can be used to enhance

affinity of negatively charged biologically active macromolecules (for instance, proteins and DNA) to biomembranes.

The work was in part supported by the Russian Foundation for Fundamental Research (grant 96-03-33725a).

## **595.E4** INFLUENCE OF STABILIZER COMPOSITION ON STABILITY AND DISPERSITY OF POLYMER ORGANOSOLS

**D.N. Yemelyanov, I.P. Lisova, Z.G. Chernorukova, N.Yu. Novospasskaya, A.I. Charov**  
*Chemistry Institute, Nizhny Novgorod State University, Nizhny Novgorod, Russia*

An aggregative and kinetic stability of polymer organosols depend on the concentration and size of particles of a dispersed phase, the structure of a diphilic stabilizer, the polarity of a medium and some other factors.

The effect of diphilic stabilizer composition on the stability of polymer organosols was studied. Particles of polymethylmethacrylate and copolymers of methacrylic acid and methacrylamide formed the dispersed phase of organosols and mixtures of precipitators for polymers acted as a medium.

A number of non-polar block and graft stabilizers based on oligourethaneacrylates having blocks of a different nature and molecular weight were synthesized.

The efficiency of a stabilizing action was estimated by the influence of stabilizer composition on their adsorption with polymeric particles, the size of the formed particles and the stability of organosols in time.

It was established that with increasing the stabilizer concentration from 3 to 7 mass % the size of particles reduces from 560 to 90 nm. A further growth of the stabilizer concentration leads to the increase of the particle size via their aggregation and to thickening and gelatinization of the dispersion.

Diagrams of stabilizer state in organic media of various polarity were obtained. It was shown that an optimal stabilizing action occurs due to the location of the stabilizer in a homogeneous region near the phase separation of a system stabilizer-medium.

An optimal mass ratio of diphilic blocks oligourethane-polyacrylate at which it is possible to prepare stable concentrated dispersions with a low viscosity and a small size of particles was found.

## **596.E4** SURFACE ACTIVITY OF DENDRIMER

**Zhang Tao, Yang Peizeng and Hsu Yong**  
*Institute of Physical Chemistry, Peking University, Beijing 100871, China*

The surface properties of half-generation starburst dendrimers (n.5-SDBs) possessing sodium carboxylated surfaces have been studied. The main findings are:

- (i) there is virtually surface activity relating to generations for some n.5-SDBs,
- (ii) higher surface activity for 6.5-SDB,
- (iii) lower surface activity for 5.5- and 7.5-SDB with respect to 6.5-SDB, which may be related to the morphology of theirs: the early generation SDBs possess shorter hydrophobic chains, the later generation SDBs are closely packed structure, which leads to the hydrophobic inner components are hard to reveal.

## **597.E5** ON THE WAVE MECHANISM OF MASS TRANSFER FOR THE ADSORPTION KINETICS IN BIPOROUS MEDIA

**Ivan I. Abarzhi**  
*Engineering Thermophysics Institute, Kiev, Ukraine*

For the first time it is proposed the principal possibility of wave mechanism of mass transfer for the adsorption kinetics in the biporous media. It is well known that the model of biporous medium is adequate



for co-polymers, etc. We consider the adsorption kinetics under the conditions of local nonequilibrium: for a small volume of the medium the rates of change of macroscopic values are comparable with the rate of local equilibrium establishment. The mass transfer under the local nonequilibrium is described in terms of phenomenological theory. The transfer wave mechanism is demonstrated by the example of adsorption in a cylindrical biporous granule. We take into account the local nonequilibrium in the both types of pores. The system of integral-differential equations describing the adsorption kinetics is deduced. It is shown that in general the system solution is defined by a parameter. This parameter is the ratio between the character relaxation time in transport pores and the character relaxation time in microporous zones. In all limiting cases of parameter value the criteria of local nonequilibrium significance for the adsorption kinetics is established. The analytical solution of the problem in various limiting cases of parameter value is found. For example, if the mass transfer in transport pores is the determining process, e.g. slowest one, the concentration distribution in biporous granule is of the form of attenuating wave. The attenuation decrement is defined by the time of local equilibrium establishment in the transport pores. At time much less then the inverse decrement the mass transfer is of the form of stable oscillatory motion. Thus, the sorption wave mechanism in biporous media is found and is defined by the conditions of local nonequilibrium in the adsorption kinetics.

## 598.E5

### THE DISSOLUBLE MATTER DISTRIBUTION IN THE BIPOROUS GRANULE UNDER THE SOLVENT EVAPORATION

Ivan I. Abarzhi

*Engineering Thermophysics Institute, Kiev, Ukraine*

It is studied the problem of the dissolvable matter distribution inside the volume of biporous granule. The problem is considered under the condition of solvent evaporation (for example, water) from the granule volume. The porous media is described as a system of plane capillaries with absorbing walls of finite thickness. The walls absorption represents the availability of microporous zones inside the granule. At initial time there is the solution inside the capillary, but there is no the dissolvable ingredient within the thickness of the capillary walls. The kinetics of the process is mainly determined by the following factors: the solvent evaporation on the open capillary side; the adsorption of the solvent vapour by the capillary walls; the adsorption of dissolvable ingredient by the capillary walls with the ingredient diffusion within the walls thickness. The solvent vapour adsorption on the capillary walls causes the film formation and influences the shifts of liquid meniscus. These effects on the kinetics coefficients values are taken into account. The dissolvable ingredient adsorption process is described by Henry law. There are some assumptions allowed one to find the analytical description of kinetics. First, we neglect the concentration difference across the capillary width. It permits one to easily formulate boundary conditions on the free liquid surface. Then, the meniscus velocity is assumed to be small and comparable with the diffusion velocities both within the walls thickness and inside the capillary volume. Under these conditions the kinetics process is quasi-steady. The distribution of dissolvable matter concentration inside the granule and other physical values of the kinetics process are found analytically.

## 599.E5

### THE INTERFACIAL AND BULK PROPERTIES OF CARBOXYMETHYLCHITIN -TETRADECYLTRIMETHYLAMMONIUM BROMIDE SYSTEM IN THE WATER AND WATER - SALT MEDIA

V.G. Babak<sup>1</sup>, G.A. Vikhoreva<sup>2</sup>, E.F. Galich<sup>1</sup>, I.G. Lukina<sup>1</sup>, N.A. Kalabina<sup>3</sup>, S.Yu. Zaitsev<sup>3</sup>,  
L.S. Galbraikh<sup>2</sup>, V.P. Zubov<sup>3</sup>

<sup>1</sup>*Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia*

<sup>2</sup>*Moscow State Textile Academy, Moscow, Russia*

<sup>3</sup>*Institute of Bioorganic Chemistry of RAS, Moscow, Russia*

The water-soluble derivatives of chitin (chitosan, carboxymethylchitin and other) are the practical use in medicine, pharmaceuticals, perfumes, and food industry. For some applications it would be rather convenient to use emulsion, micellar, and vesicular systems as well as foams containing water-soluble

polyelectrolytes in form of adsorbed layers at the surfaces of liquid and gaseous disperse particles. We investigated the modification of carboxymethylchitin (CMC) with oppositely charged ionic surfactant tetradecyltrimethylammonium bromide (TAB) and its effect on surface activity at the air/water and oil/water interfaces. Interactions between CMC and TAB, bulk and interfacial properties of formed surfactant-polyelectrolyte complexes (SPC) were studied by tensiometry, monolayer technique, viscosimetry, UV-spectrometry, elemental analysis, and by the method of contact interactions. The calculated standard free energies of adsorption  $\Delta_{ad} G^{\circ}_{298}$  per one mol of  $\text{CH}_2-(\text{CH}_3)$  groups in the alkyl radicals of cationic surfactant molecules bonded to carboxymethylchitin chains was found to be equal  $-2,4 \text{ kJ mol}^{-1}$ , that is much better than for the free ionic surfactant in the solution ( $-1,8 \text{ kJ mol}^{-1}$ ). This characteristic is independent of the ratio TAB/CMC within the range 0,001 - 1 mol/base-mol. This increment approach the corresponding magnitude of the increment that is typical for nonionic surfactants. The observed synergistic effect on the surface tension reduction, microscopic foam films, foam and emulsion stability in solutions of SPC are mainly associated with the increase in the number of surfactant molecules adsorbed at the interface in comparison with the solution of pure surfactant. The process of interaction of CMC from the bulk solution with the dimethyldioctadecylammonium bromide's interfacial monolayer was investigated also, and the substantial increasing of lipid monolayer strength in the face air/water solution resulting by the complex formation was founded.

## 600.E5 THE INTERACTION OF DIFFERENT ANIONIC SURFACTANTS WITH POLY(ETHYLENE)OXIDE

Anne Marit Blokhus and Kenneth Klokke

*Department of Chemistry, University of Bergen, Bergen, Norway*

The interaction of anionic surfactants, of different headgroups, with poly(ethylene)oxide is studied by conductivity measurements. The surfactants studied are sodium dodecylcarboxylate, sodium octylbenzenesulfonate, sodium dodecylsulfate, and lithium dodecylsulfate. The poly(ethylene) oxide used has an average molecular weight of 6000 and 35000.

By conductivity measurements the critical micelle concentration (cmc) is obtained from the break in the plot of conductivity versus surfactant concentration. In the presence of polymer the conductivity curve shows two breakpoints where the first one, called the critical aggregation concentration (cac or  $T_1$ ), signals the onset of polymer-surfactant complexation, and the second one is the surfactant concentration, ( $T_2$ ), where saturation of the polymer by the surfactant aggregates occurs.

The data obtained are discussed in terms of binding ratios (mole surfactant /mole EO) at saturation, Gibbs free energy of stabilization of the micelle by polymer complexation, given as  $\Delta G^{\circ}_{PS} = RT \ln(\text{cac}/\text{cmc})$ , and the surface ionization degree,  $\alpha$ , of free and polymer bounded micelles, estimated from the slopes of the conductivity curves. The results show that sodium dodecylsulfate interacts more strongly with poly(ethylene)oxide than the other surfactants studied and also the highest binding ratio is obtained in this case.

## 601.E5 POLYMER CONTAINING LYOTROPIC LAMELLAR PHASES: AN EXPERIMENTAL TOOL TO STUDY THE THERMODYNAMICS OF POLYMER CONFINEMENT

G  rard Bouglet and Christian Ligoure

*Groupe de Dynamique des Phases Condens  es - UMR Universit   Montpellier II/CNRS 558,  
Universit  , Montpellier II C. C. 26 F-34095 Montpellier Cedex 05 France*

We have investigated a mixed amphiphilic system formed from a brine swollen surfactant lamellar phase in between of which is incorporated a neutral water-soluble non adsorbing polymer: polyvinylpyrrolidone (PVP), with a very large molecular weight. The existence of a critical  $L\alpha/L\alpha$  phase separation is quantitatively explained by a theoretical model, we have developed, which predicts the smectic compressibility of non adsorbing polymer-containing lamellar phases, taking into account the polymer-mediated interactions between the membranes. In the case, where the lamellar phase is electrostatically stabilized, the polymer can be confined in all proportions into the lamellar phase; this allows a systematic

experimental study of the different confinement regimes of polymer solutions. The three relevant elastic constants of this mixed lamellar phase (the layer compression modulus and the two bending moduli) have been measured using different experimental techniques (SAXS, SNAS, NMR, optical microscopy). The results are compared with theoretical predictions.

## 602.E5 SURFACE INTERACTIONS OF SURFACTANTS AND CATIONIC POLYELECTROLYTES

K.E. Bremmell, S.R. Biggs, G.J. Jameson

*Department of Chemical Engineering, The University of Newcastle, Callaghan, Australia.*

Systems of mixed polyelectrolytes and surfactants and their interactions with solid surfaces are important in many technological processes and formulations where they are utilized simultaneously. Polyelectrolytes are widely used for particle growth and surfactants control surface properties at both the solid/liquid and liquid/vapour interface. The adsorption behaviour of a cationic copolymer of acrylamide and 2(methacryloxy) ethyltrimethyl ammonium chloride and ionic surfactants (sodiumdodecylbenzene sulfate and cetylpyridinium chloride) from their mixed solutions at the silica/aqueous interface as a function of concentration and order of addition are being studied. Electrophoretic mobility data, stability and flotation test results are compared with direct force measurements of the systems. The most efficient flotation occurred when the polyelectrolyte and surfactant concentration produced the least stable silica dispersion. This corresponds to the minimum in electrostatic repulsion between the flocculated particles determined from electrophoretic mobility results. These results correlate well with measured forces determined between a mica surface and a silica bead in the presence of polyelectrolyte and surfactant solutions in the direct force measurements.

## 603.E5 ENERGY CHARACTERISTICS OF THE SURFACE OF POLYSTYRENE AND POLYCARBONATE MIXTURES

A.A. Chalykh and T.I. Andreeva

*Institute of Physical Chemistry of Russian Academy of Sciences, Moscow, Russia*

The surface energy  $\gamma$  its dispersion  $\gamma^D$  and polar  $\gamma^P$  components of polycarbonate (PC), polystyrene (PS) and their mixtures of different compositions were determined by the method of contact wetting angles, using a standard set of liquids. The polymers were intermixed by the extrusion method at a temperature of 220-240 C. The energy characteristics of the surface were determined by the Owens-Vendt method. The phase structure of the polymer mixes was investigated by the method of scanning electron microscopy. It has been established that  $\gamma$  of the PC and PS depends on their density in accordance with the MacLeod equation. This, naturally, makes indefinite the interpretation of the concentration dependence of the surface energy of their mixes. It has been noted that both the dispersion and the polar component of  $\gamma$  change their values depending on the thermal conditions of the preparation of the samples. A unified tendency is observed: the higher the annealing temperature the higher the value of  $\gamma^P$ ; while a decrease in the quenching rate leads to a general increase in the value of  $\gamma$  and a decrease in the value of  $\gamma^P$ . It has been shown that these tendencies are reversible.

In the case of polymer mixes, the surface energy changes with the composition in accordance with complex curves, whose maxima are found in the region of the heterogeneous state of compositions, whereas the minima occur at the points of the compositions of coexisting phases in the diagrams of the phase state of the PS-PC system. It is essential that the polar and dispersion components also change with the composition of the system according to the curves exhibiting maximum points. It has been shown that all the noted changes of  $\gamma$ ,  $\gamma^D$ , and  $\gamma^P$  for polymer mixes occur within the admissible range of the values of energy characteristics, which is confined both on the top and below by limiting low and limiting high values of  $\gamma$ ,  $\gamma^D$ , and  $\gamma^P$  of homopolymers. It is supposed that on the intermixing of polymers, their mutual effect causes changes in both the packing density and the conformational state of macromolecules in the surface layers of the samples.

## 604.E5

ENERGY CHARACTERISTICS OF THE SURFACE  
OF EPOXY OLIGOMERS

A.E. Chalykh, V.Yu. Stephanenko, V.B. Busygin, A. D. Aliev

*Institute of Physical Chemistry of Russian Academy of Sciences, Moscow, Russia*

The method of contact angles, involving the wetting by test liquids of the surface of diene epoxy oligomers of different molecular masses, was applied to determine their surface energies ( $\gamma$ ), polar ( $\gamma_p$ ) and disperse ( $\gamma_d$ ) components. All the measurements were performed under normal conditions. For solid epoxy oligomers, the effect of the thermal prehistory of samples  $\gamma$ ,  $\gamma_p$ ,  $\gamma_d$  was investigated. The measurements of the surface characteristics of the samples were supplemented by the determination of their bulk and surface densities. For this purpose, a specially developed technique of X-ray microanalysis was applied.

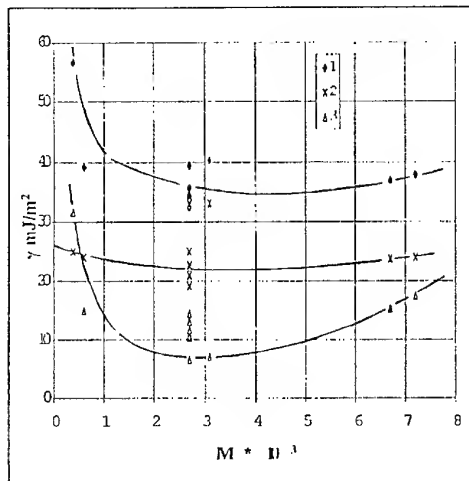


Fig. 1. Dependence of  $\gamma$  - 1,  $\gamma_p$  - 2,  $\gamma_d$  - 3 of epoxy oligomers on the molecular mass.

It is known that the concentration of end epoxy groups decreases, whereas that of hydroxylic groups increases, as the molecular mass of epoxy oligomers increases. Nonetheless, as is shown in Fig. 1, the surface energy of oligomers decreases from 51 mJ/m<sup>2</sup> for the epoxy oligomers (EO) with  $M=380$  to 32-34 mJ/m<sup>2</sup> for the EO with  $M=6500$  as their molecular mass increases. In this case, the disperse component varies but insignificantly, whereas the main changes occur in the polar component. It has been noted that the surface characteristics of high-molecular epoxy oligomers are close to  $\gamma$ ,  $\gamma_p$ ,  $\gamma_d$  of polystyrene. It is supposed that the conformational state of oligomers changes as their molecular mass increases. As a result, the surface layer is gradually enriched by aromatic radicals, contained in monomeric links. The McLeod equation was shown to be fit for describing satisfactorily the changes in the surface tension of oligomers and their density.

## 605.E5

EFFECT OF COLLOIDAL FILLERS ON CRYSTALLINE  
STRUCTURE OF PENTON AND POLYVINYLIDENEFLUORIDE

A.V. Cherenkov, S.V. Temnikova, V.M. Baranovsky, J.A. Gornostaeva

*Lugansk Pedagogical Institute, Lugansk, Ukraine*

Addition into polymers of colloidal fillers with different chemical activity, dispersion extent and particles forms is one of the most effective methods of polymer crystalline structure modification practically on all the levels of its structure. The authors have carried out a complex set of research including measurements of specific heat capacity at constant pressure, density, heat conductivity dependences on temperature and isothermal crystallization process parameters of semicrystalline samples. A number of compositions on the basis of penton and polyvinylidene fluoride structure and thermal physical properties have been studied, technical carbon, graphite and kaoline had been selected in the capacity of fillers for these compositions. It has been demonstrated that fillers particles effect on polymers structurization process is to a great extent displayed under small concentration of additions (from 0.1 to 1 mass %). According to the dependence of all the parameters studied extremes of functions correspond to this concentration range. The colloidal fillers effect leads to the transformation of both crystalline polymer fields and amorphous ones. During the crystallization process depending on fillers dispersion extent additions particles can become artificial nucleation centers (highly disperse technical carbon) or can exert influence on structurization by means of polymer layers orientation (low disperse kaoline and graphite). In amorphous fields fillers additions cause supplementary process of structure formation that leads to the essential change of composition of thermal physical properties on the whole.

## 606.E5 RHEOLOGICAL STUDY OF THE pH-DEPENDENCE OF INTERACTIONS BETWEEN GELATIN AND ANIONIC SURFACTANTS: FLOW BEHAVIOUR AND GELATION

Michael Dreja<sup>1</sup>, Kurt Heine<sup>1</sup>, Bernd Tieke<sup>1</sup> Günter Junkers<sup>2</sup>

<sup>1</sup>*Institut für Physikalische Chemie der Universität zu Köln, Luxemburger Str. 116, D-50939 Köln, Germany*

<sup>2</sup>*Agfa-Gevaert AG, Postfach 100160, D-51301 Leverkusen, Germany*

The interactions between gelatin and two anionic surfactants (sodium di-sec-butyl-naphthalene-sulfonate and sodium dodecylbenzenesulfonate, respectively) were investigated using rheological methods, charge and surface tension measurements. Upon the addition of surfactants, the viscosity of aqueous gelatin solutions increases at pH values higher than the isoelectric point (IEP) of the gelatin, provided that a distinct surfactant concentration is exceeded. The increase in viscosity depends on the structure of the hydrophobic moiety of the surfactant. Surface tension measurements indicate the formation of gelatin-surfactant-complexes. If the surfactant is added in high concentration, the viscosity does not further increase, and free micelles are formed in the solution. Directly at the IEP and at pH values below, the addition of surfactants leads to flocculation because of electrostatic interactions. At all surfactant concentrations, the flow behaviour was strictly Newtonian. As a model of the structure of the complex, a modified 'bead and necklace'-model is suggested. This model proposes the nucleation of micelles at the hydrophobic gelatin regions ('micellar surfactant gelatin complexes'). The number of micelle moieties per gelatin chain could be estimated to be about three. The complex stability is dependent on the extent of hydrophobic interaction.

The gelation behaviour of gelatin is strongly affected by the addition of the surfactant. The ratio between the attainable linear storage and loss moduli,  $G'$  and  $G''$ , decreases strongly. Gelation is generally hindered, but the effect is stronger at pH values below the IEP than above.

## 607.E5 EFFECTS OF FUNCTIONALIZED LATEX PARTICLES AND ANIONIC SURFACTANTS ON THE FLOW BEHAVIOUR OF AQUEOUS GELATIN SOLUTIONS

Michael Dreja<sup>1</sup>, Kurt Heine<sup>1</sup>, Bernd Tieke<sup>1</sup> Günter Junkers<sup>2</sup>

<sup>1</sup>*Institut für Physikalische Chemie der Universität zu Köln, Luxemburger Str. 116, D-50939 Köln, Germany*

<sup>2</sup>*Agfa-Gevaert AG, Postfach 100160, D-51301 Leverkusen, Germany*

The flow behaviour of aqueous gelatin dispersions containing latex particles with different surface characteristics is studied as a function of the concentration of anionic surfactants. The work is aimed to describe nature and strength of interactions occurring in the system. The study of the effects of individual components may help to gain information on the flow behaviour of commercial photographic colour coupler dispersions.

Due to interactions with the gelatin, the flow behaviour of a dispersion of latex particles in 4.6% (w/w) aqueous gelatin solution strongly depends on charge and surface characteristics of the particles. For hard particles with nonionic hydrophilic shell, the flow behaviour can be described by the theory of hard spheres. If anionic surfactants such as sodium i-dodecylbenzene sulfonate (DBS) or sodium di-sec-butyl-naphthalene sulfonate (BXG) are added, the rheological behaviour is mainly determined by the interactions between the gelatin and the surfactants in the continuous phase. If soft particles with ionic shell are dispersed in the aqueous gelatin, the viscosity is stronger increased than predicted by the hard sphere model. Upon further addition of a surfactant, the primarily pseudoplastic flow behaviour becomes more and more Newtonian, presumably due to depletion of originally surface-adsorbed gelatin molecules. The stabilization of the latex is changed from steric to electrostatic. If large amounts of surfactant are added, depletion flocculation is most likely to occur. A model for the gelatin-latex surfactant interactions is presented, taking in account the surface characteristics of the particles.

**608.E5****INTERACTIONS IN NONIONIC SURFACTANT-NONIONIC  
POLYMER SYSTEMS****Nicoleta Calatanu and Dan F. Anghel***Institute of Physical Chemistry "I.G. Murgulescu", Department of Colloids,  
Spl. Independentei 202, 77208 Bucharest, Romania*

Surfactants and polymers are chemical species that show marked deviation from regularity in aqueous solutions. Their unusual properties can be traced to the formation of complexes between the micellized surfactants and the polymers. Any interaction between polymer and surfactant and the property changes conferred by the resulting complexes can be of considerable practical importance. Many industrial products can be cited as examples, including foodstuffs, pharmaceuticals, cosmetics, detergents, coating fluids, inks, and paints. In nature also specific functions of membranes depend in some subtle way on the interaction between proteins and lipids.

The aim of this work was to correlate the association behaviour of polydisperse ethoxylated octylphenol (OPEO<sub>8</sub>) and its interaction with polyethylene glycol (PEG) and polypropylene glycol (PPG) in aqueous solution. The methods of investigation were surface tension, viscosity, pH and clouding point. Although the surface tension failed to detect any interaction in the OPEO<sub>8</sub>-PEG system, the other methods clearly revealed a difference between the behaviour of surfactant in the presence and in absence of polymer. For the OPEO<sub>8</sub>-PPG system, the interaction was detected by all the methods and some critical points were revealed. The binding mechanism was different for each polymer and it was mainly dependent on polymer hydrophobicity.

**609.E5****ELECTROCHEMICAL STUDIES ON CATIONIC  
SURFACTANT/POLYMER COMPLEXES IN AQUEOUS SOLUTION****Sayed Mehdi Ghoreishi, Derek M. Bloor and Evan Wyn-Jones***Department of Chemistry and Applied Chemistry, University of Salford, Manchester, M5 4WT, England*

The effective degree of micellar dissociation of tetradecyltrimethylammonium bromide (TTAB) and tetradecylpyridinium bromide (TPyB) micelles has been determined from electrochemical (emf) measurements using TTAB and TPyB selective electrodes.

The binding of surfactants TTAB and TPyB onto the neutral water-soluble hydrophobic polymers poly(propylene oxide) (PPO), poly(vinylmethylether) (PVME), ethyl(hydroxyethyl) cellulose (EHEC) and one hydrophobically modified polymer, hydrophobically modified ethyl(hydroxyethyl) cellulose (HM-EHEC) has also been investigated by the emf technique. In all cases it has been shown that the surfactant binds to the polymer and the bound surfactant exists in the form of small aggregates and three critical surfactant concentrations are observed. They are  $T_1$  the onset concentration of binding between the surfactant and the polymer,  $C_1$  at maximum  $m_1$  where the monomer concentration reaches a maximum, and  $T_2$  where polymer binding sites are completely saturated.

By measuring the EMF of the surfactant electrode relative to both sodium and bromide ions in the binding region  $T_1$ - $T_2$ , it is possible to evaluate the degree of dissociation  $\alpha$  of the polymer bound aggregate.

**610.E5****DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM  
SPECTROSCOPIC STUDY OF THE MECHANISM OF SELECTIVE SHEAR-  
FLOCCULATION OF HEMATITE FROM KAOLINITE****Gong Wenqi***Department of Resources and Environmental Engineering, Wuhan University of Technology,  
Wuhan, P. R. China*

Shear-flocculation is one of the effective processes for upgrading ultrafine mineral particles. Experiments were conducted in this laboratory to study the mechanism of separating hematite from kaolinite

by shear-flocculation. The major problem was to find out the reason responsible for the selectivity of shear-flocculation. This was solved by using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, which was found to be effective for analysing adsorbed oleate species on the highly absorbing mineral hematite.

The spectra suggest that chemisorption of oleate on hematite took place under shear-flocculation condition and that the chemisorbed species was bridged bidentate, corresponding to a peak at  $1580\text{ cm}^{-1}$ . Dimers of oleic acid, corresponding to a peak at  $1710\text{ cm}^{-1}$ , adsorbed via hydrocarbon chain association with the chemisorbed oleate. The coexistence of physically adsorbed oleic acid dimers and chemisorbed oleate ions made the surface of hematite hydrophobic, which would remain under the shear field. Under the same condition, the surface of kaolinite did not adsorb oleic acid or oleate and remained hydrophilic. The shear field of sufficient magnitude made the hydrophobic ultrafine particles of hematite to aggregate, whereas the hydrophilic ultrafine particles of kaolinite remained suspended in solution. This explains the mechanism of selective shear-flocculation of hematite from kaolinite.

## 611.E5 THE BEHAVIOUR OF SURFACTANT SOLUTIONS ON POLYMER SURFACES: WETTING AND ADSORPTION

**Ingrid Grosse and Hans-Joerg Jacobasch**  
*Institute for Polymer Research Dresden, Germany*

If a surfactant solution contacts a solid surface several events take place immediately and simultaneously: wetting of the solid - often coinciding by capillary sucking, and adsorption of the surfactant at the solid/liquid interface.

This lecture deals with results of the investigation of the wetting behaviour of surfactant solutions on flat polymer surfaces (films and foils and, in some cases textile fabrics) as well as adsorption data of different surfactants on solids with relatively high specific surfaces (fibres or powders).

The change of the advancing contact angle in time allows conclusions about the kinetics of the wetting process depending on the type and concentration of the surfactant and the polymer. In the case of capillar-porous surfaces like textiles the solution also penetrates into the spaces between the single filaments and between the threads: in addition to wetting capillary sucking takes place. The quantitative separation of both processes during wetting is rather difficult.

Measurements of the adsorbed amounts give evidences about the thickness and structure of the surfactant layers on the solid surface (mono-, multilayer). It could be shown by rewetting measurements, that the structure of these layers and thereby the surface properties of the solid change during heat treatments in dependence of the drying conditions.

## 612.E5 LIPASE - SURFACTANT INTERACTIONS

**Krister Holmberg, Martin Svensson, Britta Folmer and Brajesh Kumar Jha**  
*Institute for Surface Chemistry, P. O. Box 5607, SE-114 86 Stockholm, Sweden*

Formulations containing both surfactant and enzyme are established in the detergent area and are common also in several other applications. Proteases have been the traditional class of enzyme used in cleaning formulations but in recent years there has been a steadily growing interest in incorporating also other enzymes. Knowledge about possible interactions between enzyme and surfactant is essential in the optimisation of such systems.

We have been particularly interested in the combination of lipases and various types of surfactants. Being an enzyme with considerable surface activity, lipases can be expected to interact strongly with surfactants and such interactions are likely to affect the enzymatic activity.

Surfactant-lipase interaction has been studied both in bulk and at the solid-water and oil-water interfaces. Events at an interface are believed to be of particular relevance to lipases since this class of enzymes are known to operate at a hydrophobic surface. Surface tension measurements and ellipsometry have been the main tools in the work. Enzymatic activity has been evaluated in terms of rate of hydrolysis of a model triglyceride.

There is considerable current interest in using W/O microemulsions as minireactors for lipase catalysed lipid transformation. Proper understanding of lipase-surfactant interactions is essential in order to optimize such processes. Transesterifications, ester synthesis and ester hydrolysis have been performed in microemulsions based on different surfactants and attempts have been made to correlate reaction rate with surfactant-enzyme interactions.

## 613.E5

### EFFECT OF SOME POTENTIAL COMPATIBILIZERS ON MECHANICAL PROPERTIES OF PVC -POLYPROPYLENE BLENDS BASED ON WASTES

Mustapha Kaci

*Laboratory of Organic Materials, University of Bejaia 06000, Algeria.*

Blends of plasticized PVC and polypropylene derived from individual wastes show poor elongational characteristics owing to incompatibility [1]. It is therefore, difficult to obtain products that offer desirable combinations of characteristics by simply blending such polymers. Thus, suitably chosen additives are used to reduce interfacial tension.

In this study, two blend compositions, i.e., 80/20 and 60/40 with respect to plasticized PVC/polypropylene were used. Two types of additives were tested as potential compatibilizers; namely,

- chlorinated paraffins 700 (Chlorez 700),
- chlorinated polyethylene 48 (CPE 48).

The effectiveness of each additive was evaluated on the basis of mechanical properties, especially elongation at break, because the major deficiency of incompatible polymer blends is usually their poor ductility [2].

It has been found that the blend specimens modified with CPE 48 showed a substantial improvement of the elongation at break

1. M. Kaci, 4<sup>th</sup> Mediterranean School on Science and Technology of Advanced Polymer-Based Materials, Crete (Greece), 5-9 June 1995, pp. 367-378.
2. J. W. Barlow and D. R. Paul Polym. Eng. Sci., 21, 993 (1981).

## 614.E5

### THE EFFECT OF LINEAR POLYELECTROLYTES ON MICELLIZATION OF SURFACTANTS

Viktor A. Kasaikin

*Chemical Department of Moscow State University, 119899 Moscow, Russia*

The mechanism of micellization of cationic and anionic surfactants (S) in the presence of oppositely charged polyelectrolyte (PE) was studied using various experimental techniques (elastic and quasi elastic light scattering, ultra centrifugation, x-ray diffraction, EPR). It was shown, that in the presence of oppositely charge polyelectrolyte the surfactants micelles formed at the concentration much more lower (1-2 order of magnitude) than in the water solution of pure surfactant. The main reason of decreasing CMC is the cooperative interaction between PE and S. As result of this interactions is polyelectrolyte-surfactant complexes (PESC) formation. Depending on the condition of PE/S reaction, PESC may be as soluble, as well as not soluble in aqueous media. Phase diagram of water solutions of PESC is discussed. The transition of PESC from water-soluble into insoluble state is accompanied by the changing of composition PESC particles. As result in the concentrated phase become apparent, so called, stoichiometric complex, where the ratio of number of ionised PE-units to the number of S-ions in PESC particle is equal to 1.

It was shown, that the formation of PESC is possible only if number S ions, included in the PESC particle, sufficiently for forming intermolecular micelles in PESC particle ( $n_{min}$ ).  $n_{min}$  defined by chemical structure of PEI. In the case of PESC, formed by Sodium Polyacrylate and homologues of alkyltrimethylammonium bromide  $n_{min}$  is closed to the aggregation number of the spherical micelles of corresponding surfactants formed without PE.

PESC particles present itself self-assembling systems. It was shown, that PE determinate the morphology of micelles phase, formed in the PESC particles. In the presence of PE the morphology of



micelles change from spherical to lamellar. Notable that the morphology of intermolecular micelles does not change during of the conversion of PESC particles from water-soluble into insoluble state. The influence of S ions on the PE conformation is discussed.

The solubilization of different organic compounds by PESC was studied. It was shown, that PESC can include 2 - 3 times more of organic molecules per one S molecule than ordinary free spherical micelles formed by the same S, i.e. their sorptive capacity can be 2 - 3 times higher. Sorption of low water-soluble organics by PESC species being a cooperative process proceeds as a sharp disproportionation transition of original empty PESC species into much larger ( $10^2$  -  $10^3$  nm) aggregates saturated by absorbed organic, which then precipitate so they can be easily separated. The perspectives of PESC for water remediation is discussed.

## 615.E5

### POLYMER-COLLOID COMPLEXES: INFLUENCE OF CONCENTRATION REGIME OF POLYCATION SOLUTION ON PHASE STATE AND COMPOSITION

V.A. Kasaikin, Ye.A. Litmanovich

*Department of Chemistry, Moscow State University, 119899 Moscow, Russia*

Interaction between sodium dodecylsulfate (SDS-Na) and poly(dimethyldiallyl-ammonium chloride) (PDMDAAC) with different MW is studied in dilute and semi-dilute solutions of the polymer.

In dilute region (at polycation concentration lower than crossover concentration  $C^*$ ), nonstoichiometric polymer-colloid complexes (PCC) are shown to be formed. Ultracentrifugation data shows that the process is accompanied by disproportionation of the system onto free polycation and PCC of constant composition  $\phi_{ch}=0.4$ . Variation of the reaction mixture composition  $Z$  at  $Z < \phi_{ch}$  leads only to change in relative amounts of free polycation and PCC of composition  $\phi_{ch}$ . Molecular characteristics of this PCC are obtained by means of light scattering. Particles of PCC of composition  $\phi_{ch}$  are shown to form in solution asymmetrical associates with mean radius of gyration  $R_g \sim 70$  nm. At  $Z > \phi_{ch}$ , insoluble products of composition  $\phi = 1$  are formed. At  $Z = 1$ , PDMDAAC and SDS-Na are quantitatively bound into insoluble stoichiometric complex.

In semi-dilute solutions of polycation (at  $C > C^*$ ), the reaction between PDMDAAC and SDS-Na leads to formation of thixotropic gel. Viscosity of the gel increases on increase in SDS-Na content in the mixture. Syneresis of the gel is observed at  $Z > \phi_{ch}$ , the volume of concentrated phase being decreased on increase of  $Z$ . At  $Z=1$ , the gel becomes fully contracted, no components of PCC being observed in the solution.

The mechanism of polymer-colloid reaction at different concentration regimes is discussed.

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## 616.E5

### STATIC- AND DYNAMIC LIGHT SCATTERING ON SEMIDILUTE AQUEOUS SYSTEMS OF A NONIONIC CELLULOSE ETHER. EFFECTS OF TEMPERATURE, SURFACTANT AND SALT

Anna-Lena Kjøniksen and Bo Nyström

*Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern, N-0315 Oslo, Norway*

Static- and Dynamic Light Scattering experiments have been carried out on thermoreversible gelling and nongelling semidilute aqueous systems of ethyl(hydroxyethyl)cellulose (EHEC) (at a constant polymer concentration of 1 wt %) in the presence of various amounts of sodium dodecyl sulfate (SDS) and at some different levels of NaCl addition. Depending on the concentrations of surfactant and salt, a temperature-induced sol-gel transition or only a viscosification of the solution was observed.

The time correlation data, obtained from the dynamic light scattering experiments, revealed the existence of two relaxation modes. The "fast" mode is always diffusive, i.e.,  $q^2$ -dependent ( $q$  is the wave vector), and exhibits an exponential profile. The "slow" mode can be represented by a stretched exponent,

and it displays a more complex  $q$ -dependence. Both the "fast" and the "slow" relaxation modes, are shown to change with the concentration of salt, surfactant addition, and with temperature.

The reduced inverse scattered intensity function,  $S(0)/S(q)$ , gained from the static light scattering experiments, displays a  $q$ -dependence that is varying with temperature and with the amount of salt and surfactant. The effects of temperature, salt and surfactant addition on the correlation length are also discussed.

## 617.E5

### INTERACTIONS OF ACETYLENIC DIOL SURFACTANTS WITH POLYMERS

**R. Krishnan and R. Sprycha**

*Sun Chemical Corporation, 631 Central Ave., Carlstadt, NJ 07072, USA*

Surfactants are widely used in the Graphic Arts Industry. In water based liquid inks surfactants are added to lower the surface tension of the ink, to help its spreading on the substrate surface, and improve color development. Low foaminess of the printing inks is a very important factor. Only a few commercially available surfactants can offer very low dynamic surface tension and simultaneously very low foam. Surfynol surfactants, by Air Products, based on acetylenic diol chemistry are examples of a very effective and low foam surface active agents. It was found recently that non-ionic acetylene diol surfactants can interact with some polymers used in printing ink formulations. The purpose of this paper was to study in more systematic way the interactions of acetylenic diol surfactants (of different HLB values) with some polymers used in liquid inks (e.g. acrylics, maleics, polyamides). The interactions were studied by surface tension measurements. The Dynamic Surface Tension (DST) of the surfactant solutions, polymer solutions, and solutions of polymers and surfactant at different polymer/surfactant ratios were measured using differential maximum bubble pressure technique (Sensadyne 6000 instrument). Acetylenic diol surfactants interacted quite strongly with some polymers (e.g. water soluble acrylic polymers) forming weakly surface active complexes. This undesirable phenomenon is responsible for higher than expected doses of these surfactants needed to keep the DST of the inks low enough.

## 618.E5

### THE RECOVERY OF OMETHOATE FROM OMETHOATE WASTE WATER BY SURFACTANT-PRECIPITATION METHOD

**Xue-gang Li, Chang-bin Shu**

*Southwest Agricultural University, Centre Laboratory, Chong Quing 630716, China*

The precipitation takes place when anionic and cationic surfactant solutions are mixed. Similarly, the precipitation takes place when ionic surfactant is combined with some opposite-ionic substance such as protein or organic substance. This can be used to recover some worthy substance from waste water and decrease or even eliminate pollution.

## 619.E5

### ADSORPTION AND MECHANICAL PROPERTIES OF MIXED PROTEIN/SURFACTANT SYSTEMS AT THE WATER/AIR INTERFACE

**A.V. Makievski<sup>1,2</sup>, J. Krägel<sup>3</sup>, M. Bree<sup>1</sup>, R. Wüstneck<sup>3</sup>, R. Miller<sup>1</sup> and V.B. Fainerman<sup>2</sup>**

<sup>1</sup>*MPI for Colloids and Interfaces, Rudower Chaussee 5, D-12489 Berlin, Germany*

<sup>2</sup>*Institute of Technical Ecology, 25, Boulevard Shevchenko, Donetsk, 340017, Ukraine*

<sup>3</sup>*University of Potsdam, Institute of Solid State Physics, Rudower Ch. 5, D-12489 Berlin, Germany*

The dynamic properties of protein/surfactant interfacial layers have impact on many technologies, such as food technology, cosmetics, coating, pharmaceuticals. A number of effects cannot be reached by proteins or surfactants alone. Complicated mixtures of surfactants do not allow to replace proteins, and also proteins or their mixtures are not able to form interfacial layers with a certain required behaviour. Mixtures

of polymers and low molecular weight surfactants represent exactly the kind of systems which can provide a very special dynamic interfacial behaviour. Such systems have quite a large capacity due to the large range of variations in the nature of the components and their composition.

Using a number of instruments protein/surfactant model systems are studied. The adsorption behaviour is measured via dynamic and equilibrium surface tensions (drop volume method and pendent drop technique). The data are discussed on the basis of thermodynamic and kinetic models. The dilational rheology is investigated by the pendent drop technique using drop volume jumps to generate surface tension relaxations. The dilational elasticity and viscosity are obtained as functions of surface coverage and composition of the interfacial layer. These data are compared with results from ellipsometric studies of the interfacial layer thickness.

The results are discussion in terms of competitive adsorption of the protein and surfactant molecules depending on the chemical nature of the components and their composition. Examples of different strength of interaction are given and the consequences in the interfacial behaviour discussed.

## 620.E5 ASSOCIATION OF SAS MICELLES WITH POLYELECTROLYTES

**Musabekov K.B., Abilov Zh.A., Tazhibaeva S.M.**

*AI-Faraby Kazakh State National University, Almaty, Kazakhstan*

The processes of association of micelle forming surface active substances with opposite charged polyelectrolytes are investigated. The associates with regulated hydrophilic-lipophilic balance and phase state are obtained. Quantitative evaluation of electrostatic contacts being formed between SAS micelles and polyelectrolytes functional groups and hydrophobic interactions stabilizing these bonds is given. It is shown that in dilute solutions of SAS the value of electrostatic interactions degree doesn't exceed 20-25 %, then in micellar systems it increases up to 95 %. The increase of hydrophobicity of polymer chains and decrease of charge density being observed at their interactions with opposite charged SAS ions result in considerable change of macromolecules conformation. In connection with this investigation of conformation state of polyelectrolyte macromolecules in the micellar system is of great interest. It is stated that the viscosity of micellar solution has tendency to decrease with the increase of polymer concentration. This is due to the change of energy balance of SAS nonpolar radicals hydrophobic interactions and solvation of polar groups as well as the energy of electrostatic repulsion of SAS ions to the increase of hydrophobic interactions. The effect of pH on association process is investigated. It is shown that changing pH medium one can displace the equilibrium of reaction in necessary direction. According to the electrophoretic investigations data the charge of associates of micelles with polyelectrolytes is determined. Regions of existence of stoichiometric polyelectrolytic complexes of SAS are stated. It is shown that phase state of associates depends on ratio between polyelectrolytes and SAS, sequence of mixing of components. The obtained results can be used for separation of SAS ions from sewage.

## 621.E5 INTERACTIONS BETWEEN NONIONIC POLYMERS AND SDS: SOME KINETIC ASPECTS.

**Livio Persi, Alessandro D'Aprano and Camillo La Mesa\***

*Dipartimento di Chimica, Università "La Sapienza", P. le Aldo Moro 5, 00185 Roma, Italy*

The kinetic properties of the systems water /SDS /PVP, (M.W. $\approx 3 \cdot 10^4$ ), water /SDS /PEO, (M.W. $\approx 1 \cdot 10^5$  and  $\approx 2 \cdot 10^5$ , respectively) and water /SDS /PPO, (M.W. $\approx 1.5 \cdot 10^3$ ), were investigated by different ultrasonic relaxation methods, between 1 and 100 MHz, as a function of polymer and surfactant concentration, at 25° C. In systems containing constant amounts of PVP, or PEO, three different regions are observed: i) one where the relaxation time,  $\tau_1$ , increases with increasing the SDS content; ii) a region where  $\tau_1$  is nearly constant and iii) a third region where  $\tau_1$  decreases on increasing the amount of surfactant. The above features are ascribed to the presence of a non interaction region, at low SDS content, to surfactant ion binding on the polymer backbone, at intermediate content, and to micelle formation, respectively. In some cases two well separated relaxation processes were observed. In the system water /SDS/PPO no interaction regions have been observed and the system behaves in analogy with pure SDS micelles. A comparison

between the kinetic behaviour of systems with and without polymer allows to determine the width of the interaction region, which depends on the polymer wt% in the mixture. From the above data a phase diagram has been drawn and the number of surfactant ions bound to the polymer,  $\langle m \rangle$ , evaluated. A thermodynamic model based on the above results allows to calculate the Gibbs energy of binding on the polymer,  $[\Delta G_{\text{bind}}/\langle m \rangle]$ ; the resulting value is close to that inferred from standard thermodynamic investigations. The volume change of micelle formation,  $\Delta V_{\text{mic}}$ , and of surfactant binding on the polymer,  $\Delta V_{\text{bind}}$ , respectively, have been evaluated from the corresponding ultrasonic relaxation amplitudes: the volume of binding is lower than that of micellization.

## 622.E5 MECHANISM OF THE ADHESION INTERACTION OF THE TYPE METAL-RUBBER-RUBBER. EFFECT OF THE MIGRATION OF INGREDIENTS

T.F. Petrova

*Institute of Physical Chemistry of Russian Academy of Sciences, Moscow, Russia*

It has experimentally been established that the strength of an adhesive joint in the system made up of steel-rubber 1-rubber 2, where the rubber 1 (R1) is adhesive, and the rubber 2 (R2) the substrate, depends both on the contents and the nature of the ingredients and water, contained in the R2. The R1 was prepared on the basis of oligomeric nitrile rubber with  $-\text{COOH}$  end groups. In the case of R2, the samples were tested of the rubbers of standard compositions, prepared on the basis of high-molecular rubbers, such as ethylene propylene, butadiene nitrile, and fluororubber. The methods of analytical electron microscopy have shown that the failure of the joints was of the cohesive character. The failure of the joints occurred predominantly along the adhesive layer (R1). On the lamination of the joints, the mouth of crack shifted over the cross section of the R1 depending on the distribution and composition of the ingredients in the adhesive layer.

The profiles of the distribution of the ingredients and water were investigated by the methods of high-power liquid chromatography in combination with the layerwise preparation of R1 and R2. Simultaneously, the density of the space network in the rubbers was measured, and the parameters of the interaction of the components with the rubbers were calculated.

It has been shown that the thermodynamic affinity of the ingredients with the rubbers is the moving force of the migration process. Calculations have demonstrated that the migration processes can be stopped by adding special ingredients to the compositions of the substrate and adhesive, the additions equalizing the difference in chemical potentials. This allows for obtaining stable values of the strength of the adhesion interaction between R1 and R2, too.

## 623.E5 EFFECT OF SURFACTANT ON THE POLYMER ADSORPTION ON METAL OXIDE PARTICLES

Polunina I.A.

*Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia*

The adsorption of some polymers on the porous and nonporous disperse metal oxides modified by different surfactants has been investigated.

At first, it was studied the individual adsorption of the surfactants (stearic acid - SA, and octadecylamine - ODA) and two polymers (copolymer of vinylchloride, vinylacetate and maleinic acid - VMCH, and polystyrene - PS) on the nonporous  $\text{TiO}_2$  (rutile,  $7 \text{ m}^2/\text{g}$ ) and on the porous aluminosilicagel (ASK,  $300 \text{ m}^2/\text{g}$ ). Both the surfactants can chemically react with active sites of  $\text{TiO}_2$  and ASK. The VMCH adsorption was partially irreversible on the metal oxides surface. The PS adsorption was reversible, and it had negative magnitude for ASK.

So, for nonporous rutile the increasing degree of surface modification by surfactants ( $x$ ) leads to the decreasing of the polymer adsorption. But when  $x=0.2$  the polymers adsorption remarkably increases owing to the dispersity rise of  $\text{TiO}_2$  particles.

The PS adsorption on ASK modified by surfactants becomes positive one, and it has a high value. The surfactant molecules, probably, penetrate into the pore space and activate the hydrophylic surface of the ASK particles with respect to polymer medium, moreover there are sufficiently surface active sites for polymer adsorption on porous adsorbent surface.

## 624.E5

### POLYMER-SURFACTANT INTERACTION STUDIES IN AQUEOUS SYSTEM

**Anuradha Rangaraj and Animesh kumar Rakshit**

*Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002, India*

Polymer-surfactant interaction studies have been carried out between the nonionic polymer Polyacrylamide (PAA) and cationic surfactant Cetyl trimethyl ammonium bromide (CTAB). The experiments performed were surface tension, conductance and viscosity at various temperatures of 30, 35, 40 and 45°C. As usual two critical concentrations were observed, one was below the normal aqueous critical micelle concentration of the surfactant (CAC) and the other above it (PSP). The critical aggregation concentration (CAC) and polymer saturation point (PSP) respectively were computed. Both CAC and PSP were found to decrease with increase in temperature. The increase in polymer concentration on CAC values seems to be irregular whereas PSP shows a dip around 0.001 wt% polymer, particularly at 40 and 45°C. The degree of ionization ' $\alpha$ ' of the polymer-surfactant complex was computed from the slope of the conductance-surfactant concentration plot below and above the PSP. With increase in temperature, ' $\alpha$ ' was found to increase. However, with increase in polymer concentration, the ' $\alpha$ ' showed a minimum at around 0.001 wt% polymer concentration. The thermodynamic quantities i.e. free energy, enthalpy and entropy changes associated with the PSP were also computed. The associated entropy changes were reasonably highly positive for all systems at around 120 JK<sup>-1</sup>mol<sup>-1</sup>. The enthalpy changes at PSP show exothermic nature with a value of around 1 kJmol<sup>-1</sup>. The surface excess quantities of the surfactant solution at PSP were also computed and was found to increase with increase in temperature. The intrinsic viscosity of the polymer at 3 different surfactant concentrations were taken and was found to increase with increase in concentration indicating higher interaction at higher concentration. With increase in temperature the intrinsic viscosity shows a maximum around 35°C at all surfactant concentrations. This indicates more structure formation in the system around that temperature.

## 625.E5

### THE EFFECT OF NON-IONIC EMULSIFIER TYPE ON THE EMULSION POLYMERIZATION OF VINYL ACETATE

**Ayfer Sarac<sup>1</sup>, Hüseyin Yildirim<sup>1</sup>, H. Yildirim Erbil<sup>2</sup>**

<sup>1</sup>*Yildiz Technical University, Faculty of Sciences, Department of Chemistry, 80270 Sisli, Istanbul, Turkey.*

<sup>2</sup>*TUBITAK, Marmara Research Center, Department of Chemistry,  
P.O. Box 21, 41470 Gebze Kocaeli, Turkey.*

Vinyl acetate homopolymerization were performed using a series of ethoxylated (EtO) nonyl phenol non-ionic emulsifiers and partially hydrolyzed polyvinyl alcohol as protective colloid in a semi-continuous monomer addition system.

10, 20, 30, 40 and 50 mole ethoxylated nonyl phenol emulsifiers were used. Homopolymerizations were carried out as two sets. In the first set, constant emulsifier weight % recipes, thus decreasing molar % with the increase of (EtO) content, were used. In the second set, constant emulsifier molar % recipes, thus increasing weight % with the increase of (EtO) content, were used.

The viscosities of 50 % solid contents lattices, particle size distributions, molecular weights of benzene soluble homopolymer and the surface free energies of the dried latex films by contact angle goniometry were measured. The effect of both the emulsifier concentration and (EtO) content on the particle size, molecular weight and film surface energetics were examined. It was determined that for constant molar % recipes; the increase of (EtO) content of the emulsifier resulted in increased mean particle sizes, increased polymer molecular weights and decreased latex viscosities.

## 626.E5

INTERACTION BETWEEN POLYCARBOXYLIC ACIDS  
AND SURFACTANTS BASED ON POLY(ETHYLENE GLYCOL)

S. Shenkov, V. Doseva, V.Yu. Baranovsky

*Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The interaction between synthetic polyelectrolytes and surfactants (Sf) in aqueous solutions has been of great interest because these reactions could be used as a simple model of more complicated interactions between natural electrolytes and the membranes of living cells or physiologically active substances with surface active properties. Synthetic polyelectrolytes have been finding wider application in different colloid-chemical processes (flocculation, solubilization, stabilization of different dispersions).

The interaction between polymethacrylic (PMAA) and polyacrylic (PAA) acids and micelle forming alkyl, naphthyl and *tert*-butylphenyl monosubstituted poly(ethyleneglycol)s (PEGs) in aqueous solution have been studied viscometrically and by potentiometric titration. The reaction runs in two stages with increasing Sf concentration. At lower Sf concentrations the polycomplexes (*PMAA-Sf*) or (*PAA-Sf*) are formed. The molecular structure of Sf in the polycomplex depends on its hydrophilic-hydrophobic balance. Sf macromolecules can either form linear sequences of hydrogen bonds between the oxygen atoms of PEG and the hydrogen atoms of the nondissociated carboxylic groups of the polyacid, or incorporate themselves in the polycomplex as micelles. At higher Sf concentrations the polycomplex bounds additional amounts of Sf and a hydrophilic associate between the polyacid and the micelles of Sf is formed. A hypothetical model of this hydrophilic associate has been suggested.

## 627.E5

INTERACTION OF POLY-L-LYSINE  
WITH SURFACTANT MONOLAYERSL.V. Sigolaeva<sup>1</sup>, A.A. Yaroslavov<sup>2</sup>, I.N. Kurochkin<sup>1</sup><sup>1</sup>*Chemical Enzymology and* <sup>2</sup>*Polymer Science Departments, Faculty of Chemistry,  
Moscow State University, Moscow, 119899 Russia*

Traditionally phospholipids monolayers on the air-water interface have been considered as a rather simple but convenient model of cell membranes suitable for the investigation of polyelectrolyte/cell membrane interactions. Studying of this process is very important because it allows to control membrane density and microstructure.

For the understanding of the molecular mechanisms of the formation of polymermonolayer complexes the interactions of poly-L-lysine (PL) with monolayers composed from the mixtures of phosphatidylcholine (PC) - cardiolipine (CL) and phosphatidylcholine - stearic acid (SA) were studied by Langmuir film-balance experiments.

Surface pressure-area isotherms of monolayers deposited on subphase without polyelectrolyte were firstly investigated. It was shown that isotherms of pure PC, CL or SA monolayers have typical shape and arrangement, described elsewhere. Varying the PC/CL and PC/SA ratio two series of isotherms were obtained with a consequent transition from isotherm typical for pure PC to that for pure CL(SA) without any other particularities.

The properties of the monolayers mentioned above formed on the surface of PL containing buffer subphase at zero surface pressure condition were studied. The considerable expansion of the monolayer expressed in the shift of the surface pressure area isotherms to the region of higher surface areas were observed both for PC/CL and PC/SA system. Whereas PL solutions as it was examined does not show ally surfactant activity. There is no any expansion also when pure PC is deposited on the PL solution. It was found that the degree of monolayers expansion increases when the concentration of negatively charged surfactant is raised, moreover in the case of PC/SA system this dependence is linear. The maximal effect was equal to 150 % of increase of the surface area per surfactant molecule in our experiments.

Thus it seems to be reasonable to conclude that the expansion of monolayers is mainly due to the strong electrostatic interaction between the positively charged polymeric units of PL macromolecules and the negatively charged CL (or SA) heads. The correlation between mean distances among positive charges in the polymeric unit and the negative ones located in the monolayer are quite responsible for such effects. The

former is nearly constant, the latter strictly depends on the charge concentration and the external surface pressure (i.e., the degree of monolayer compression).

## 628.E5 THE INTERACTION OF SODIUM CARBOXYMETHYLCELLULOSE WITH SURFACTANT

Verica Sovilj and Petar Dokic

*Faculty of Technology, Bul. cara Lazara 1, 21 000 Novi Sad, Yugoslavia*

The interaction between polyelectrolyte and surfactant in solution has been subject of intense research, because of great importance in many processes in food, pharmaceutical cosmetic and chemical industry. In contrast to the interaction between nonionic polymer and ionic surfactant the interaction between polyelectrolyte and oppositely charged surfactant is dominated by strong electrostatic forces, even though hydrophobic interaction may play a secondary role too. The polymer conformation also undergoes the changes upon binding of surfactant. If the system include strong polyelectrolyte and oppositely charged surfactant when the concentration of surfactant is increased, electrostatic interaction causes irreversible precipitation of the complex polyelectrolyte-surfactant.

In this paper interaction between the anionic polyelectrolyte - sodium carboxymethylcellulose (NaCMC) and cationic surfactant cethyltrimethylammonium bromide (CTMAB) has been investigated by viscosity measurements. Most of the investigations involve systems with surfactant concentrations below or not much higher than critical micellar concentration (CMC) of the surfactant. In order to provide precipitation of the complex at concentration of surfactant much above CMC, the binding strength was reduced by addition of salt (NaBr) and nonionic surfactant (tween 80). The changes in viscosity of NaCMC in salt solution at various CTMAB concentrations and in presence of nonionic surfactant added in different way were measured. Also, as the measures of conformational changes of NaCMC molecule during interaction, intrinsic viscosity, equivalent hydrodynamic radius and end to end distance were calculated.

## 629.E5 COMPLEXATION AND FILM FORMATION IN STARCH/SURFACTANT SYSTEMS

Per Stenius, Juha Merta and Terhi Saarinen

*Laboratory of Forest Products Chemistry, Helsinki University of Technology Espoo, Finland*

Cationic starch (CS) forms complexes with anionic surfactants (alkanoates and sodium dodecyl sulphate) in dilute aqueous solution. At CS/surfactant charge equivalence a hydrophobic CS/surfactant complex phase (gel) separates. The water content of the gel depends on the hydrophobic/hydrophilic balance of the surfactant. It is therefore of interest to understand how complexation and gel formation is affected by surfactant mixtures.

Surface tension and viscosity measurements were used to investigate micellisation of mixed anionic surfactants and CS/surfactant interactions. Gel particle charge and gel structure was studied by determination of electrophoretic mobility, phase equilibria and the rheology of the gel phase.

Micellisation in systems containing surfactants of different chain length shows a distinct synergism when the molar ratio of long chain to short chain soaps is 3:1. This is probably due to optimal packing of the monomers in mixed micelles. The interaction between surfactant mixtures and CS results in gel separation at very low concentrations. The interaction is governed by the more hydrophobic surfactant. The gel always contains more long-chain than short-chain surfactants. The water content of the gel increases and the viscosity decreases when the fraction of short-chain surfactant increases. Reduction of the molecular mass of the starch does not affect the interactions, but markedly reduces the viscosity of the gel.

The results are interpreted in terms of current theories of mixed micelle formation. They show that the interaction parameter is particularly strong when the molar ratio of the long and short chain surfactants is 3:1

When dried, the gels form remarkably hydrophobic films. Some studies of the structure of these films will be described.

**630.E5 INTERACTION BETWEEN ELASTIN AND SALTS OF FATTY ACIDS****J. van Vreeswijk, J. Lyklema, W. Norde***Department of Physical and Colloid Chemistry, Wageningen Agricultural University,  
POB 8038, 6700 EK Wageningen, The Netherlands*

Elastin from bovine ligamentum nuchae is incubated in aqueous solutions of sodium salts of fatty acids (FAS) at pH 7 and 70° C. The FAS are laurate, myristate and palmitate. Adsorption of FAS in the elastin network is studied as a function of time, FAS concentration and ionic strength. The rate of absorption follows a second order binding mechanism, where the rate constant increases with decreasing length of the FAS. Absorption of FAS strongly increases the swelling of the elastin. This is ascribed to an osmotic pressure primarily caused by the concomitant uptake of low molecular weight ions. The pressure induces a slow degradation of the elastin, i.e. a decrease in the cross link density. As a result, the elasticity modulus of elastin decreases. The absorption equilibrium is described by the Langmuir theory. The absorption affinity increases with increasing hydrocarbon chain length of the FAS, indicating the contribution of hydrophobic interaction between FAS and the hydrophobic side groups along the polypeptide chains. In line with this, both stress-strain and glass transition measurements indicate that the binding of FAS does not significantly affect the conformational states of the polypeptide main chains in the elastin network.

**631.E5 A SPECTROFLUORIMETRIC STUDY OF PROTEIN-SURFACTANT  
INTERACTION IN BOVINE SERUM ALBUMIN-SODIUM DODECYL SULFATE  
AQUEOUS SOLUTIONS****Daniel Angelescu, Marilena Vasilescu***Institute of Physical Chemistry I.G.Murgulescu, Splaiul Independentei 202, 77208 Bucharest, Romania*

The interaction of bovine serum albumin (BSA) - sodium dodecylsulfate (SDS) and the resulted complex were investigated by spectrophotometric measurements at two pH values: close to the isoelectric point of the protein or to the physiologic conditions. The specific interaction brings about a denaturation of the protein which is evidenced by changes in UV-VIS absorption and fluorescence intensities. The ratio between the first and third vibronic peaks, I<sub>1</sub>/I<sub>3</sub>, and the fluorescence lifetime of pyrene give information with respect to the interaction between the protein and the surfactant, above and below CMC value. It was found out that the CMC of the surfactant does not change in presence of the protein. The aggregation number of SDS, determined by the method of static quenching of pyrene fluorescence, is smaller than the number corresponding to free micelles and varies with the increasing of the protein over surfactant concentration ratio; the values agree to those obtained by other methods. The variation of aggregation number as well as of pyrene fluorescence lifetime support the "necklace" complex structural model which suggests that along the unfolded protein micelle-like clusters are formed.

**632.E5 MICROCAPSULES FORMATION BASED ON PROTEIN-  
SURFACTANT INTERACTIONS****Yelena Vinetsky, Shlomo Magdassi***Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, 91904, Jerusalem Israel*

A method for obtaining microcapsules of oil droplets by formation of insoluble protein - surfactant complex is described and consists of two parallel stages: study of the protein - surfactant interactions, and the use of the insoluble protein - surfactant complexes, during a microencapsulation process.

Two types of gelatin, which are positively or negatively charged at suitable pH range, were studied in order to form insoluble complexes with an anionic surfactant, Sodium Dodecyl Sulphate (SDS) and with cationic surfactants, Dodecyltrimethylammonium Bromide (DTAB) and Cetyltrimethylammonium Bromide (CTAB).



It was found that at each pH value, addition of surfactant to the protein solution lead to formation of a turbid solution only at specific surfactant concentration range. Therefore it was explained that performing the microencapsulation processes, which are based on precipitation of gelatin by surfactants, should be conducted at very specific pH and surfactant concentration.

Hydrophobicity of the gelatin-SDS complexes was evaluated by contact angle measurement. It was found that at the protein/surfactant molar ratio which leads to the insoluble complex formation the contact angle with water is maximal and, therefore, the complex is more hydrophobic.

As was verified by light microscope and scanning electron microscope (SEM), microcapsules were obtained only at specific surfactant concentration/pH combinations. This concentration range corresponds to the surfactant concentration at which the highest turbidity and, respectively, the insoluble protein-surfactant complex (without oil phase), is observed.

Both the amount of gelatin and surfactant bound to the oil-water interface were maximal in the precipitation range in agreement with zeta potential measurements and fluorescence microscopy performed for Fluorescein Isothiocyanate (FITC) labeled gelatin. This maximum corresponds to the same SDS concentration range which leads to formation of microcapsules.

Several crosslinkers were tested for hardening of the microcapsule walls and allow it's easier removal from the solution. Addition of redispersion aids such as Manitol, CMC, PEG and Silica led to prevention of microcapsule coalescence and to obtaining microcapsules in a powder form. These microcapsule powders were easily redispersed in aqueous solutions.

### **633.E5 PULSED FIELD GRADIENT NMR STUDY OF POLY(ETHYLENE OXIDE) DIFFUSION IN AQUEOUS SOLUTIONS AND GELS**

**Harald Walderhaug, Anna-Lena Kjøniksen, and Bo Nyström**

*Department of Chemistry, University of Oslo, P. O. Box 1033, Blindern, N-0315 Oslo, Norway*

Tracer diffusion of monodisperse fractions of poly(ethylene oxide) (PEO) with molecular weights ranging from  $1.2 \cdot 10^5$  to  $1 \cdot 10^6$  in aqueous mixtures of ethyl(hydroxyethyl)cellulose (EHEC) and sodium dodecyl sulfate (SDS) at different temperatures has been studied by pulsed field gradient NMR. In semidilute solutions of EHEC in the presence of moderate SDS concentrations and probe amounts of PEO, the systems form thermoreversible gels at elevated temperatures. The results show that there is only a modest obstruction effect of the probe chains as the gel evolves, while the probe diffusion is slowed down as the EHEC concentration increases. At high surfactant concentration, the network structure is disrupted and probe diffusion increases.

In the presence of ionic surfactants, the strong interactions between EHEC and surfactant give rise to electrostatic interactions, and the bound ionic surfactant endows an apparent polyelectrolyte character to the initially nonionic EHEC. In order to study how the interaction situation changes, tracer diffusion measurements have also been carried out in the presence of various amounts of salt. The overall picture that emerges from this investigation is that the diffusion of PEO chains is affected by factors such as the matrix concentration, surfactant concentration, length of the probe chains, and salinity. These tracer diffusion results can provide useful insights into the network structure of EHEC as well as the interaction between cosolutes and EHEC.

### 634.F1 DETERMINATION OF THE WATER BOUNDARY LAYERS THICKNESS AND THE SURFACE CHARGE OF A $\text{SiO}_2$ PARTICLE ACCORDING TO THE DATA OF THE OSMOTIC PRESSURE AND ELECTROOSMOTIC MEASUREMENTS

O.L. Alexejev, Yu.P. Boyko, V.N. Shilov, N.I. Zharkich

*Biocolloidal Chemistry Institute UAS of Ukraine, Vernadsky av. 42, 252142, Kiev, Ukraine*

Many authors have recorded high values of the osmotic pressure ( $\pi$ ) caused by disjoining pressure in the concentrated but unaggregated systems under the conditions of strong double electric layer (DEL) overlap. In such systems the volume fraction ( $\phi_f$ ) of the boundary layers (BL) of the bound water which substantially worse than usually dissolves substances including the DEL counterions is also high. From the known expressions for the disjoining pressure, Donnan's equilibrium and the density of the volume charge ( $\rho$ ) in the DEL overlaps we obtain:

$$\pi = 2RTC_0 \left\{ \left[ (\rho / 2FC)^2 + 1 \right]^{0.5} - 1 \right\}$$

If  $h$  is the BL thickness,  $a$  is the colloid particle radius, ( $\phi$  is the colloid particle volume fraction  $\phi_f = 1 - (1 + h/a)^3 \phi$ . From the electroneutrality conditions it follows:  $\rho \phi_f = 3\sigma / a$ , ( $\sigma$  is the density of the particle surface charge). After identical transformations in order to receive the  $\phi$  linear function in the right side we have:

$$3 / 2FaC_0 \left[ \left( \pi / 2RTC_0 + 1 \right)^{0.5} - 1 \right] = 1 / \sigma - (1 + h/a)^3 \phi / \sigma.$$

If the dependence of the left part of the equality on  $\phi$  is linear this means strong overlap of the diffuse layers of the counterions their uniform space distributions and the possibility to determine  $h$  and  $\sigma$  was received experimentally with LUDOX-the  $\text{SiO}_2$  sol with the spheric particles of the radius  $a=6.0$  nm and  $C_0=0.01\text{M}$ . The linearity of the right part of the equality versus (in the interval  $\phi=0.198+0.277$ ) has been established and  $h=2.6$  nm and  $\sigma=0.094$  C/cm<sup>2</sup> have been calculated as a result of the osmotic pressure measurement at various  $\phi$  values. Practically the same result ( $h=3.1$  nm) was obtained by electroosmotic technique.

### 635.F1 THE EFFECT OF VARIOUS ELECTROLYTES ON THE ZETA POTENTIAL OF PARAFFIN PARTICLES DISPERSED IN WATER

Mikael Alfridsson<sup>1</sup> and Staffan Wall<sup>2</sup>

<sup>1</sup>*BIM Kemi AB, Stenkullen, Sweden*

<sup>2</sup>*Department of Physical Chemistry, University of Göteborg and Chalmers University of Technology, Göteborg, Sweden*

The electrokinetic (zeta) potential was measured as a function of electrolyte and concentration. Three different salts were used; NaCl, NaBr and NaI. The paraffin particles were suspended in water and behenic acid was used as an emulsifier together with ammonia. The electrokinetic properties were studied by means of electroacoustic and electrical conductivity measurements. The result was that the zeta potential increased initially with increasing salt concentration and then decreased in the same manner as has been reported for latex particles though the proposed mechanism is different.

### 636.F1 INVESTIGATION OF THE MECHANISM OF ELECTROSTATIC CHARGING OF POLYMERS

A. Augsburg, F. Simon, H.-J. Jacobasch

*Institute of Polymer Research, Hohe Str. 6, 01069 Dresden, Germany*

The electrostatic charging caused by charge transfer between insulating materials like polymers during contact have been widely utilized in industry, e.g. in the electrostatic separation process of polymer waste and the electrophotography. The electrification mechanism is not sufficiently understood. The

formation of a donor-acceptor interaction with transferred electrons and an ion transfer mechanism during the contact is discussed. The electrification process is an effect taking place on the surface as recent investigations have shown. The magnitude and sign of electrostatic charging of polymers depend significantly on surface properties caused by the chemical constitution of the surfaces (functional groups on the surfaces, unsaturated bonds, impurities, adsorbed surface layers). These characteristics ask for extensive spectroscopical and thermodynamical investigations of polymer surfaces.

In this respect, ESCA (electron spectroscopy for chemical analysis) is used to elucidate qualitative and quantitative composition and to identify functional groups on polymer surfaces. Very often both surface and bulk phase have a different composition caused by interfacial oxidation and ageing processes.

With IGC (inverse gas chromatography) the adsorption of vapour probes is utilized to investigate the specific interactions of a solid-vapour-system. The technique allows the evaluation of the thermodynamical parameters of polymer surfaces and enables the characterization of the surface according to the Lewis electron donor-acceptor concept.

Zetapotential measurements are used to determine the Brönsted acid-base interaction, that means the  $pK_a$  and  $pK_b$  values of the surfaces. The pure polymers investigated included powders of polyvinylchloride, polyethylene and polyamide. In this presentation we have shown how the sign of electrostatic charging of polymers is correlated with surface properties, which were characterized by ESCA, IGC and zetapotential measurements.

## 637.F1 THEORY OF ELECTROSTATIC DISPERSION OF POLYMER SOLUTIONS IN AIR FOR PRODUCTION OF HYDROGEL MICROBEADS CONTAINING BIOCATALYST

Valery Babak<sup>1</sup>, Denis Poncelet<sup>2</sup>

<sup>1</sup>INEOS RAS, 28 Vavilova str., Moscow 117813 Russia

<sup>2</sup>ENSAIA, BP. 172, 54505 Vandoœuvre, France

Immobilization of living cells and enzymes inside the hydrogel beads may be realized by the so-called dropping method consisting in the formation of droplets by pumping polymer solution containing bioactive substances through a needle and then solidifying the falling droplets in a receiving solution via ionotropic or termotropic gellation, or interpolyelectrolyte complex formation. The major drawback of the dropping method is the relatively large bead size (greater than 1 mm) and the low rate of the bead formation.

Significant decrease of the droplets size (much lesser than 1 mm) may be achieved via applying an electric potential between the needle and the receiving solution. The characteristic features of the electrostatic dispersion of polymer solutions is a gradual decrease of droplets diameters  $d$  with increasing applied difference of potentials  $U$  up to some critical value  $U_{cr}$  and formation of instable liquid jets which disaggregate in multiple droplets with diameters lesser than 0,1 mm in the region of  $U > U_{cr}$ . The droplets diameter  $d$  as well as the critical difference of potentials  $U_{cr}$  depend on numerous physico-chemical parameters such as internal diameter  $d_c$  of capillary, viscosity  $\eta$  and surface tension  $\sigma$  of polymer solutions, size and electric charge of counter-ions and macroions, flow rate  $j_v$  of polymer solution, polarity of applied electric potential, geometry of dropping set-up, and so on.

We have developed a theory of electrostatic dispersion of polymer solutions in air which is based on the electrochemical phenomenon of decreasing the surface tension with increasing the surface density of electric charge (Lippman's law). We have obtained for the critical difference of the electric potential the expression:

$$U_{cr} = k \cdot (d_c \sigma_0 / \epsilon_0)^{1/2},$$

where  $\sigma_0$  is the surface tension at  $U=0$ ,  $\epsilon_0$  is the dielectric permittivity of vacuum,  $k$  is the parameter which value depends on the characteristic time  $\tau_{ad}$  of adsorption of surfactants species and the characteristic time  $\tau_v$  of formation of liquid droplets. The droplets diameters decrease with increasing  $U$  as:

$$d = d_0 [1 - (U/U_{cr})^2]^{1/3},$$

where  $d_0$  is the droplet diameter at  $U=0$ . The theoretical curves  $d(U)$  fit well the corresponding experimental dependences obtained for the alginate hydrogel microbeads containing biocatalysts in different mentioned physico-chemical conditions.

The decrease of droplets size with increasing  $U$  in the region  $U > U_{cr}$ , where a single jet splits in multiple threads of small droplets, is described in the range of the suggested theory by the instability of the

surface (Raleigh) undulatory motion of termofluctuation nature. The probability of formation of an instable fluctuation which transforms in a jet with the diameter  $d_j$  sharply increases when the electrostatic pressure  $P_{el} = \zeta \cdot E$  (where  $\zeta$  is the surface density of the electric charge,  $E$  is the intensity of the electric field) becomes greater than the capillary pressure  $P_{rc} = 4\gamma/\lambda$  created by the fluctuation with the wave length  $\lambda$ , or when  $d_j = \lambda > 4\gamma/\zeta \cdot E$ .

## 638.F1

### SUPERFAST ELECTROPHORESIS OF ELECTRON-TYPE CONDUCTING DISPERSED PARTICLES

Sandor Barany<sup>1</sup>, Natalia Mishchuk<sup>2</sup>, Andrey Tarovsky<sup>2</sup> and Ferenc Madai<sup>1</sup>

<sup>1</sup>University of Miskolc, 3515 Miskolc-Egyetemvaros, Hungary

<sup>2</sup>Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, 252680 Kiev, 42 Vernadsky blvd. Ukraine

Superfast electrophoresis is a new electrokinetic phenomenon theoretically predicted by S.Dukhin and N.Mishchuk, and firstly observed for ion-exchanger particles in our Laboratory at the Institute of Colloid and Water Chemistry, Kiev; it was further investigated at the University of Miskolc.

It has been shown that the velocity of electrophoretic movement of large graphite, activated carbon and Al/Mg alloy particles (diameter, 100-1000  $\mu\text{m}$ ) as well as carbon fibres in strong electric fields (100-500V/cm) exceeds the well known electrophoretic velocity values typical for non-conducting particles by two orders of magnitude. It means that the so-called superfast electrophoresis or electrophoresis of the second kind observed by us for ion-type conducting (cation or anion exchanger grains) particles and fibres, is realized also for particles with electron-type conductivity.

The electrophoretic mobility of particles investigated increases not only with the external electric field but also with the size of particles or length of fibres. The mobility of such particles or fibres depends on the conductivity ratio between the particles and the medium, and it does not depend on the structure of the electrical double layer. This is in contrast to classical electrophoresis.

The conditions for superfast electrophoresis of electron-type conducting particles are examined theoretically. The superfast electrophoresis occurs only in the case if electrochemical oxidation-reduction reactions take place at the particle surface. The potential drop on particles has to be high enough to ensure the decomposition of electrolytes, and thus reach the regime of over-limit current. This is required for the formation of space charge near the surface that is a precondition for superfast electrophoresis to occur. A relationship is presented between the superfast electrophoretic velocity and the size of conducting particles, outer field gradient, electrolyte decomposition voltage and solution parameters.

We developed a new method for investigation of superfast electrophoresis in electric field pulse regime. An image analyzer equipment SIS V3 and a Leitz Panphot macrophotographer connected with a video-recorder was used for measuring of the electrophoretic velocity of particles. Using this method the size of particles and their lateral drift, i.e. their deviation from the normal sedimentation trajectory in electric field, were measured on the summarized image analyzer with high accuracy.

## 639.F1

### LOW FREQUENCY DISPERSION OF SURFACE CONDUCTING PARTICLES AS MEASURED BY MEANS OF ELECTROROTATION

H. Bäumlér<sup>1</sup>, B. Neu<sup>1</sup>, R. Georgieva<sup>1,2</sup>, V.N. Shilov<sup>3</sup>, E. Knippel<sup>4</sup>, A. Budde<sup>4</sup>, E. Donath<sup>4</sup>

<sup>1</sup>Institute of Transfusion Medicine and Immunohematology, Medical Faculty Charité, Humboldt University of Berlin, D-10098 Berlin, Germany

<sup>2</sup>On leave from Trakian University, Stara Zagora, Bulgaria

<sup>3</sup>Inst. of Biocolloid Chemistry, Kiev, Ukraina

<sup>4</sup>Dept. of Internal Medicine, Div. of Clinical Research, University of Rostock, Germany

Electrorotation is a dielectric spectroscopic technique capable of measuring the polarizability of single particles recorded as a function of the frequency of the applied rotating electric field. Red blood cells have been investigated by means of electrorotation in the frequency range of 16 Hz to 30 MHz. In the low frequency range (16Hz-2kHz) additional effects appear which are still not completely understood. Glutaraldehyde fixed red blood cells show in the low frequency range their first cofield rotation peak. A

possible cause for this additional cofield rotation could be electroosmosis while the second peak appears due to the Maxwell-Wagner effect. For this type of cells different conductivities of the external medium between 1.0 mS/m and 18.5 mS/m and the dependence of the surface charges on this cofield rotation by means of neuraminidase treated red blood cells were investigated. The rotation speed first increases with increasing external conductivity up to a maximum rotation speed around 3.5 mS/m and decreased with further increase of the external conductivity. A decreasing surface charge density led to a reduction of the rotation speed in the low frequency range. The position of the peak remained to be unaffected by the surface charge density. However, it was not possible to observe this low frequency effect with native red blood cells which show the typical counter- and cofield rotation spectrum due to the interaction of the induced dipole and the rotating electrical field or rather a Pauli-Schwan dispersion.

## 640.F1 A PERTURBED ELECTRIC DOUBLE LAYER NEAR THE CHARGED MEMBRANE WITH SINGLE PORE

M.L. Belaya<sup>1,2</sup>, V.G. Levadny<sup>1,3</sup>, and V.F. Aguilera<sup>1</sup>

<sup>1</sup>Universidad Jaume I, 12080 Castellón, Spain,

Permanent addresses: <sup>2</sup>Institute of Plant Physiology, Russian Acad. of Sci., Moscow, Russia,

<sup>3</sup>The Scientific Council for Cybernetics, Russian Acad of Sci., Moscow, Russia.

If the permeability of an membrane's pores is enough high and/or there is the single pore in the membrane, the rate with which ions is going from the solution bulk at the entrance of the pore influences on the total conductivity of the membrane system very much and can become the rate-determining step. In the present study we have considered the movement of percent ions in the aqueous solution converging from bulk toward the entrance of the single conducting pore placed into the charged lipid membrane. The aim of the study is to determine the distribution of the electric potential and the ion's concentration profiles in electrolyte in the vicinity of the pore under steady-state conditions. Moreover the specific attention has been paid the analysing of the membrane surface charges on these profiles. The 3-D Poisson's equation has been used for description of the electric potential profile in the solution. The dependence of the concentration profiles of each ion on the electric potential has been obtained on the base of the Nearest-Planck's equation. We have obtained the analytical solution of the considered problem. In order to get this one the electric potential and ion fluxes have been suggested to be small. The dependencies of the potential and the ion's concentration profiles in electrolyte on such parameters of the considered systems as electric current, membrane surface charge density, pore permeability and permselectivity, has been analyzed. These profiles strongly depend on the direction of the ion's fluxes, and hence the potential and concentration distributions on the both sides of the same membrane with the single channel are significantly different. Our solution transforms to Gouy-Chapman's theory at far separation from the pore entrance. In nearest vicinity of the pore the mentioned above profiles are close to radial symmetrical ones, but the significant influence of the membrane surface charges is also continued here. We also have analyzed the influence of the membrane surface charges on the "access resistance" in the diffusion-limited case. It turned out these charges accelerate the total ion flux at one side of the membrane (e.g. decrease the access resistance) and in the same time damp it at another side.

## 641.F1 A PERTURBED ELECTRIC DOUBLE LAYER NEAR THE CHARGED MEMBRANE WITH HIGH DENSITY OF THE PORES

M.L. Belaya<sup>1,2</sup>, V.G. Levadny<sup>1,3</sup>, and V.F. Aguilera<sup>1</sup>

<sup>1</sup>Universidad Jaume I, 12080 Castellón, Spain,

Permanent addresses: <sup>2</sup>Institute of Plant Physiology, Russian Acad. of Sci., Moscow, Russia,

<sup>3</sup>The Scientific Council for Cybernetics, Russian Acad of Sci., Moscow, Russia.

We have considered the distribution of the electric field near the charged and neutral membranes with the pores. The relationship between potential and ion concentration has been obtained in framework of the perturbation approach to the nonequilibrium Double Electric Layer where zero approximation is the classical Gouy-Chapmann's theory. We have taken into account the next, first order correction. Besides, we

have added the standard Goyu-Chapmann's theory by the term that takes into account the average pore resistivity  $r_{ch}$ .

On the base of the developed theory we have considered the electrical profile in the solutions, voltage drop on the membrane, access resistance and apparent I-V curve of the system. We have shown the electric profile is depended essentially on the relationship between the pore's  $r_{ch}$  and solution's  $\rho$  resistivities. For charged membrane in certain cases the profile becomes non-monotonical. It can result in sedimentation of molecules with small concentration fraction (e.g. impurities, drugs, anaesthetics, etc.) on membrane and pore's entrance. As voltage drop on the membrane we have shown the importance of taking into account mentioned above first correction to Goyu-Chapmann's theory in case not very concentrated solution. Without this one the error in estimation of the voltage drop can be 50% and more. We have considered also access resistance and apparent I-V curve of the total system "electrolyte-membrane - electrolyte". The access resistance is determined by pores's and solution's resistivities, surface charges density and Debye's length of the solution. The same is related to the apparent I-V curve.

## 642.F1

### A PERTURBED ELECTRIC DOUBLE LAYER NEAR A SOFT POLAR INTERFACE

Marina Belaya<sup>1</sup>, Vicente Aguilera<sup>2</sup>, and Victor Levadny<sup>2</sup>

<sup>1</sup>Permanent Adresses: Institute of Plant Physiology, Russian Academy of Sciences

<sup>2</sup>Departamento de Ciencias Experimentales, Universidad Jaume I, 12080 Castellón, Spain

A perturbation analysis is applied to a nonequilibrium double electric layer (NDEL) near a membrane with extended soft permeable interfaces (polar zones) under steady-state ion flux conditions. The membrane has been modelled as composed of three layers: an inner hydrophobic layer and two polar zones with fixed charges and dipoles. Ion flux is described according to Nernst-Planck and Poisson equations. A first order approximation of the nonequilibrium electric potential has been obtained, using the electric current as the small parameter. The influence of the ionic flux, the surface dipole density and the thickness of the polar zone on the NDEL near the membrane has been analysed. The electric potential and hence the ion concentration profiles in the NDEL change considerably with surface dipole density. A maximum in the electric potential, which is determined by ion flux and polar zone parameters, is predicted in certain cases. The effects shown can help in the interpretation of permselectivity measurements.

## 643.F1

### THE INFLUENCE OF THE DISPERSE SYSTEM FIXED CHARGE ON THE ION MOBILITY. STRONG OVERLAP OF THE DOUBLE LAYERS

Mykola P. Bondarenko, Vladimir N. Shilov

*Institute of Biocolloidal Chemistry of National Academy of Sciences of Ukraine, Kyiv, Ukraine*

In disperse systems the mobile ions have to overcome or to round the potential barriers appearing due to inhomogeneous charge distribution. As a result their effective mobility proves to be less as compared with that in a free electrolyte. A decrease in the diffusion coefficients is higher in the absence of inexchangeably sorbed electrolyte when the screening is exclusively performed by counter-ions. At high electrolyte concentrations the fixed charges are screened and do not affect the ion movement.

There are many reasons for the fact that the fixed charge distribution in homogeneous: the charge step-type behaviour, spontaneous change of the distances between the charges, disposition of the fixed charges on the interface etc. The modern theoretical models separate any one peculiarity of the charge distribution. So, the model of the charged cylinders (Las G. Nilsson et al. J. Phys. Chem., v.89, #15 p. 3385) or spheres (B. Jonsson et al. Colloid & Polymer Sci., v. 264, # 1, p. 77) allows to take into account that the charges is concentrated along a macroion or on the surface of a micelle and the model of the heterogeneous ionite (Gnusin N.P., Grebenuk V.D., Lebedev K.A.) takes into consideration the increased charge density in the gel phase. We shall give the assessment of the contribution of different peculiarities in the diffusion coefficient decrease. If a conduction is no strongly changes from point to point and the distribution of the sections with the changed conduction is isotropic, the cubic root against the medium conduction is equal to the average value of the cubic root of the system conduction. The distribution of the equilibrium ion concentrations is determined from the Poisson-Boltzmann equation.

$C_x$ mol/l	Cell model	Lattice	Random
10	0.3507	0.3418	0.1498
1	0.8389	0.8349	0.7311
0.1	0.9625	0.9613	0.9150
0.01	0.9916	0.9913	0.9731
0.001	0.9996	0.9996	0.9973

in this case is minimum. On the other hand, the spontaneous deviation of the charge density are important in case of not very high capacities.

As an example we shall give the dependence of a relative decrease in the diffusion coefficient,  $D_m/D_0$ , for different models of the disposition of the discrete fixed charges against the exchange capacity,  $C_x$  ( $c_0 = 0$ ). The diffusion coefficients for the cell model and the cubic lattice are practically equal. At high concentration they are close to the results obtained for chaotically disposed charges: the influence of the spontaneous changes in the charge density

## 644.F1 INVESTIGATION OF THE ELECTROLYTIC CODEPOSITION OF OXIDES WITH COPPER

J. P. Celis<sup>1</sup>, C. Dedeloudis<sup>1</sup>, M. Jaskula<sup>2</sup>, P. Nowak<sup>3</sup>, J. Hotlos<sup>2</sup>, N. Spyrellis<sup>4</sup>, J. Macheras<sup>4</sup>, C. Kollia<sup>4</sup>, S. Psarrou<sup>4</sup>, V. Terzieva<sup>5</sup>, M. Kaisheva<sup>5</sup> and L. Terziev<sup>5</sup>

<sup>1</sup>Catholic University of Leuven, Department of Metallurgy and Materials Engineering,  
B 3001 Leuven, Belgium

<sup>2</sup>Jagiellonian University, Department of Physical Chemistry and Electrochemistry, 30-060 Krakow, Poland

<sup>3</sup>Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 30-239 Kracow, Poland

<sup>4</sup>National Technical University of Athens, Chemical Engineering Faculty, Athens 153 73, Greece

<sup>5</sup>Faculty of Chemistry, University of Sofia, Sofia 1126, Bulgaria

The electrochemical synthesis of composite coatings consists in incorporating small particles suspended in an electrolytic plating bath into the metal matrix during metal electrodeposition. Such coatings have a considerable interest for their specific properties, like wear resistance, corrosion resistance, etc. In the present work the conditions and the possibility of the electrolytic synthesis of Cu-SiO<sub>2</sub> and Cu-TiO<sub>2</sub> composite coatings have been investigated. Copper an interesting matrix metal for composite coatings, since copper is used in electrical applications in which wear-resistant properties become more and more important. Such composite coatings containing oxide particles are, however, very difficult to be obtained from conventional acidic copper plating baths. Rotating disk electrode, rotating cylinder electrode and stationary electrodes have been used for that purpose. The influence of different surface-modifying agents on the codeposition process has been studied. The synthesis, surface treatment and characterization of silica powders has been investigated as well. Copper-silica composite plating has been carried out by DC, pulse and pulse reversed current technique, on a rotating disk electrode, in the presence of thiourea or BRIJ30. The crystallographic texture of the deposits has been investigated by X-ray diffractometry. Codeposition of the system Cu-TiO<sub>2</sub> was performed by varying the following parameters: bath composition, type of TiO<sub>2</sub>, presence of other electrolytes (Na<sub>2</sub>SO<sub>4</sub>, KNO<sub>3</sub>), TiO<sub>2</sub> concentration in the bath. The influence of some additives has been tested as well. Results will be presented on the dependence of the weight percentage of oxides in the coating as a function of the dispersion concentration. Scanning electron micrograms of the coatings and of their cross-sections have been taken. Friction coefficients of the coatings have been determined as well.

## 645.F1 CHARGE OF EMULSION DROPLETS IN THE PRESENCE OR ABSENCE OF NONIONIC SURFACTANTS

N. D. Denkov<sup>1</sup>, K. G. Marinova<sup>1</sup> and R. P. Borwankar<sup>2</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, Faculty of Chemistry,  
Sofia University, 1126 Sofia, Bulgaria

<sup>2</sup>KRAFT General Foods, Inc., Technology Center, 801 Waukegan Road, Glenview, IL 60025, USA

The electrophoretic mobility of oil droplets dispersed in electrolyte solution was measured in two types of experiment: (i) in the absence of any surfactant, and (ii) in the presence of nonionic surfactants Tween 20, Span 20 and ultra-pure C<sub>16</sub>EO<sub>8</sub>. In case (i) four different oils were used. Special precautions were undertaken to avoid artefacts caused by the presence of ionic surfactant impurities. One of them was the

development of an original procedure for production of xylene-in-water emulsions by consecutive heating and cooling the system. In this way finely dispersed, evenly sized emulsion droplets were produced. Samples prepared in this way were of highest purity as they came into contact only with parts made of glass, which were carefully pre-cleaned. The results show that the oil droplets are negatively charged and the magnitude of their  $\zeta$ -potential strongly depends on pH and the ionic strength of the aqueous phase even in the absence of surfactants (1). The electrophoretic mobility was almost independent on the specific non-polar oil at similar conditions. Series of experiments were performed to check different possible hypotheses about the origin of the spontaneous charging of the oil-water interfaces. The results lead to the conclusion that the negative charges originate from the adsorption of hydroxyl ions, released by the dissociation-association equilibrium of the water molecules. The experimental data are interpreted by using Stern's adsorption isotherm and the specific adsorption energy is estimated to be 25 kT per hydroxyl ion (kT is the thermal energy). The magnitude of this energy suggests that the adsorption is connected to an energetically favorable process of hydrogen bonds formation between the hydroxyl ions and the water molecules at the interface. The measurements in the presence of nonionic surfactants demonstrated decrease in the magnitude of the  $\zeta$ -potential upon increase of the surfactant concentration. This means that the nonionic surfactants modify the electrostatic potential at the oil-water interface, rather than to create it, as thought previously. The results show that complete theoretical description (e.g., thermodynamic one) and modelling of the oil-water interface cannot be achieved without taking into account the spontaneous adsorption of hydroxyl ions. Experiments with batch emulsions and emulsion films were performed to demonstrate that the electrostatic interactions play a substantial role in the properties of emulsions stabilized by nonionic surfactants at low ionic strength.

1. K. Marinova, et al., "Charging of Oil-Water Interfaces Due to Spontaneous Adsorption of Hydroxyl Ions" *Langmuir* 12 (1996) 2045-2051.

## 646.F1 THE NONLINEAR HAIR LAYER THEORY OF ELECTROPHORETIC FINGERPRINTING

E. Donath, A. Budde, E. Knippel

*University of Rostock, Dept. of Internal Medicine, Clinical Research, Rostock, Germany*

Electrophoretic fingerprints are three-dimensional representations of the mean electrophoretic mobility of particles or cells versus pH and conductivity. For the calculation of electrophoretic fingerprints of large particles with charged layers, a numerical procedure has been developed which incorporates nonlinearity, local surface charge isotherms, steric exclusion of ions from charged surface layers, hydrodynamic flow penetration into the charged layer, as well as a surface conductivity correction for surfaces with highly charged layers. The theory has been applied to consecutive charged layer by layer polymer adsorption onto latex particles.

## 647.F1 THEORY OF THE THERMOVOLTAGE IN STM ON A Cu(111) 2x1 MISSING ROW STRUCTURE

D. Drakova<sup>1</sup> and G. Doyen<sup>2</sup>

<sup>1</sup>*University of Sofia, Institute of Physical Chemistry,*

<sup>2</sup>*University of Munich*

We present the results of scattering theory on thermovoltage in the scanning tunneling microscope (STM) on the 2x1 missing row reconstruction of Cu(111) in comparison with the results concerning the STM and the ST spectra. Tunneling via surface resonance states at the Fermi level is suggested as the cause for the "inverted" thermovoltage and STM images compared to a topographic image of the reconstructed copper surface.



## 648.F1 SURFACE AND DIPOLE POTENTIALS – THE EFFECT OF INORGANIC CATIONS OF HIGH AFFINITY TO THE LIPID MEMBRANE INTERFACE

Ermakov Yu.A.

*A. N. Frumkin Institute of Electrochemistry, RAN, Moscow, Russia*

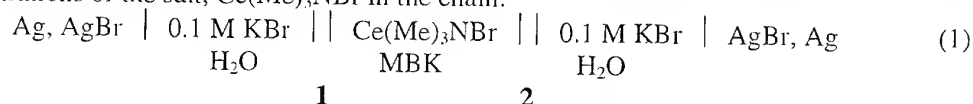
The inorganic cations of high affinity to the lipids,  $\text{Be}^{2+}$  and  $\text{Gd}^{3+}$  are known as the nonspecific blockers of the mechanosensitive channels in the cell membranes and their activity is supposed due to lipid reorganization in the biomembranes. The adsorption of these cations on the lipid surfaces was studied by the measurements of electric field distribution at the membrane/water interface composed by phosphatidylserine (PS), phosphatidylcholine (PC) and PS/PC mixtures. The measurements were made by three methods: a) the Intramembraneous membrane Field Compensation (IFC) developed for planar bilayer lipid membranes (BLM) and sensitive to any changes of boundary potential; b) electrokinetic measurements of liposomes sensitive to diffuse (surface) component of this potential and c) the simultaneous measurements of Volta-potential and surface pressure-surface area diagrams of the lipid monolayers. The quantitative description of potential drop in the diffuse part of double layer was based on the Gouy-Chapman-Stern theory modified by condition of mass balance, essential for cations of high affinity to the surface. It was shown that these cations induces the changes in boundary potentials (and Volta-potential) which are much higher than ones in the surface (or zeta) potentials. The dipole potential changes were calculated from the experimental data by modified theory. The value of dipole potentials were found about 40 mV for  $\text{Be}^{2+}$  and 140 mV for  $\text{Gd}^{3+}$  at their surface concentration above the point of zero surface charge. The induced dipole potentials are correlate with the presence of PS in the PS/PC mixtures and PS state of ionization at different pH. The structural changes of membrane/water interface and lipid clusterization are discussed in respect of their biological importance.

## 649.F1 THE LIQUID/LIQUID INTERFACE IN THE EXTERNAL ELECTRIC FIELD

V.N.Golubev

*Institute of Food Industry, Moscow, Russia*

The effect of electric current on interface properties has been studied with the 0.1M KBr/Ce( $\text{Me}$ )<sub>3</sub>NBr (cetyltrimethylammonium bromide) solutions in MBK (methylbutylketone) as an example. The experiments consisted in obtaining the voltage-current characteristics of the water/MBK interface at various concentrations of the salt, Ce( $\text{Me}$ )<sub>3</sub>NBr in the chain:



The changes in interphase tension at the interface can be described by the Sand equation:

$$C(0, t) = \frac{C(0) + 2(T_m^- - T^-)}{(\pi D)^{1/2}} I t^{1/2}, \quad (2)$$

where  $T_m - T$  is the difference between the numbers of transfers across the interface and in the organic phase volume.

Analysis of effects of electric current on interphase tension revealed that values of it remained constant within a broad range of current densities 10-750  $\mu\text{A}/\text{cm}^2$ , thus suggesting a possibility of applying equation (2) to the water/MBK interface. The diffusion coefficient for Ce( $\text{Me}$ )<sub>3</sub>NBr in MBK calculated from this equation is equal to  $6 \times 10^6 \text{ cm}^2/\text{sec}$ .

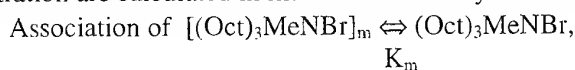
Thus, the experimental data reflecting the effects of electric current on the properties of the interface: KBr in  $\text{H}_2\text{O}$ /Ce( $\text{Me}$ )<sub>3</sub>NBr in MBK are satisfactorily described by diffusion kinetics equations on the assumption that the electrochemical characteristics of the interface are similar to those of the ideal ion-exchange membrane.

## 650.F1 EFFECT OF ASSOCIATION OF AMMONIUM SALTS IN BENZENE ON SURFACE ACTIVITY

V.N. Golubev

*Institute of Food Industry, Moscow, Russia*

The characteristic S-shape of all surface pressure isothermal curves for alkylammonium salts in benzene is due to their association in media with low dielectric permeability (for H<sub>2</sub>O-saturated benzene  $\epsilon=2.453$ ). This phenomenon reminds, in many features, of micelle formation in the aqueous phase, however, the number of monomers (ion pairs) in the associate formed by alkylammonium salts in benzene is rather low (2-32). Stipulating that association in solution is the chief cause of the abnormal shape of surface pressure isotherms, the latter can be used for calculating activity coefficient for alkylammonium salt solution. If it is granted that the ability to be absorbed at the interface is unique for monomers (this conjecture is tantamount to stating that association is the sole cause of the activity coefficient deviation from unity), the monomer concentration may be calculated from surface pressure isotherms. Monomer concentration are calculated in much the same way as activity coefficients are.



where  $K_m$  is the equilibrium constant.

The mean aggregation number for the (Oct)<sub>3</sub>MeNCl concentration range of  $10^{-3}$  to  $2 \times 10^{-2}$  M is eight which agrees well with the results obtained by other methods. Calculation of aggregation numbers from surface produce an opposite dependence. The possible reason for such discrepancy is that the activity coefficient for the salts associated in a great degree (nitrate, iodide, perchlorate) at a site where the derivative, reaches maximal values, is below unity, i.e. association in solution does take place. Hence, before calculation activity coefficients from surface pressure isotherms, it is necessary to determine, using an independent method, the activities corresponding to the maximal packing of the monolayer which significantly demerits the method.

## 651.F1 THE ADSORPTION PHENOMENA DURING POLAROGRAPHIC REDUCTION OF COPPER IONS

Z. Görlich, M. Jaskula

*Department of Physical Chemistry and Electrochemistry, Jagiellonian University, 30-060 Cracow, Poland.*

The organic substances present in the solution may influence the kinetics of electrode process in various way. One of the most important is their adsorption on the electrode. We investigated the surface activity of aliphatic alcohols in the system:  $10^{-3}$  M Cu<sup>2+</sup> in 0.5M H<sub>2</sub>SO<sub>4</sub> containing: 0-70% vol. of methanol, 0-30% vol. of ethanol, 0-25% vol. of propanol, 0-7% vol. of butanol and 0-1% vol. of amyl alcohol. The measurements were performed using D.C.- and A.C.-polarography and tensammetry. The presence of alcohols influences on the shape of polarograms and may be attributed to the following effects: 1) change of solution structure, 2) change of the character of the diffusing ion, 3) change of the structure of electrical double layer on the electrode/electrolyte interface. The bulk parameters are responsible for behaviour of Cu(II) ions during the reduction process in the range of the limiting currents where the products  $I_d \eta^{1/2}$  are constant. The surface activity of alcohols influencing the change of the electrical double layer structure, appears as additional lowering of the limiting current (D.C. polarography) and as the decreasing of differential capacity (tensammetric curves), in the adsorption potential ranges. Taking into account arelative decrease of the capacity, it is possible to evaluate the electrode surface coverage, the potential of the maximum adsorption, and the values of the maximal lowering of the d.l. capacity. The presence of alcohols in the supporting electrolyte does not disturb the reduction potential of the Cu(II) ion by their surface activity, because even for the most active alcohol i.e.n-pentanol, the range of adsorption potentials, does not attain this value. However activation energy of the process of Cu(II) ions reduction decreases in the investigated systems as indicate the shifts of the  $E_{1/2}^{Cu}$ -values towards the less negative potentials in the methanolic, ethanolic and partially propanolic solutions. This effect was ascribed to an increase of the activity of the electrolyte, which then promotes the adsorption of SO<sub>4</sub><sup>2-</sup> anions and enhances the reaction of C.T. But this is significant for higher concentrations of alcohols.

The use of above mentioned methods allowing for tracing the electrode reaction, as well as the adsorption processes and the changes in medium viscosity enabled to estimate the contribution of the particular factors in the Cu(II) ion reduction.

## 652.F1

### ELASTIC MODULI OF CHARGED MEMBRANES- CHANGES IN IONISATION DURING BENDING

Martin Hoffmann and Sylvio May

*Institut für Biochemie und Biophysik, Friedrich-Schiller-Universität, Jena, Germany*

Recently, progress has been made in assigning the electrostatic contribution to the curvature elastic moduli  $k$  and  $\bar{k}$  [1] of charged amphiphilic membranes [2-4]. It has now become clear that membrane surface charges may contribute considerably to the elastic membrane behavior [5-9]. So far, changes in ionization during bending, which are of importance for highly charged membranes, have not been taken into account. Here, we present partially analytic results for  $k$  and  $\bar{k}$ , firstly under the condition that the surface charge density is fixed during bending and, secondly, that changes in ionization can take place through a finite dissociation constant  $K$ .

Chain, interfacial and steric headgroup repulsion terms are included using mean-field chain statistics and the opposing forces model. The calculations are performed for mono- and bilayer membranes and are compared to current experimental studies on microemulsions [10,11].

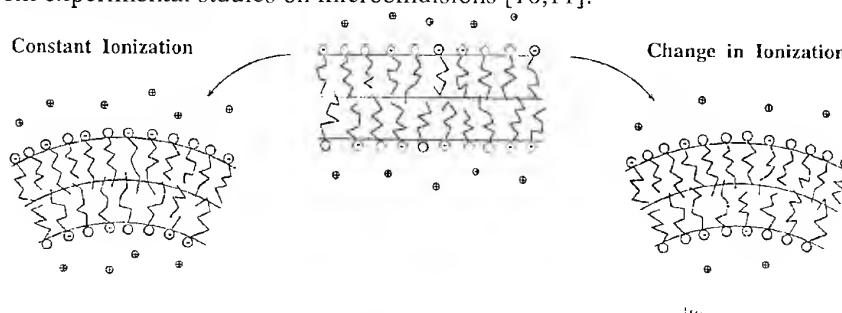


Fig.: Constant and variable headgroup ionization during bending.

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## 653.F1

### ADSORPTION OF A CHARGE-REGULATED PARTICLE TO A CHARGED SURFACE

Jyh-Ping Hsu and Yung-Chih Kuo

*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617, R.O.C*

The adsorption of a spherical particle coated with an ion-penetrable membrane to a charged surface immersed in an electrolyte solution is analyzed. The former, which simulates a biological particle, is capable of regulating the degree of dissociation of the functional groups in the membrane as a response to the variation in the electrical condition of the surrounding medium. The membrane contains both acidic and

basic functional groups, and a general form for each is assumed which allows multiple-proton transfer among functional groups. Two classes of nonuniform distribution for the functional groups are considered. We show that the more concentrate the functional groups are distributed near the outer boundary of the membrane, the greater the electrostatic repulsion force between the particle and the surface, and the slower the rate of adsorption. Compared with a rigid particle carrying the same numbers of acidic and basic functional groups, the existence of the membrane has the effect of increasing the rate of adsorption. The electrostatic repulsion force between a particle with membrane and a rigid surface is smaller than that between a rigid particle and a rigid surface if the separation distance is greater than a critical value. The reverse is true if the separation distance is smaller than the critical value.

## 654.F1 DOUBLE LAYER CHARGE DISPLACEMENT BY CELL ADHESION

Nadica Ivosevic<sup>1</sup>, Solveg Kovac<sup>1</sup>, Vera Zutic<sup>1</sup>, Ralph Lewin<sup>2</sup>

<sup>1</sup>Center for Marine Research, Rugjer Boskovic Institute, Zagreb, POB 1016, 10001 Croatia

<sup>2</sup>Marine Biology Research Division, Scripps Institution of Oceanography University of California, San Diego, La Jolla, CA 92093-0202, USA

We report the electrical attachment signals recorded in laboratory cultures of marine microflagellates and bacteria. The attachments signals are current-time transients caused by a displacement of double-layer charge at the electrode/aqueous electrolyte interface by cell adhesion during the initial attachment and spreading of a cell. Marine microflagellates with fluid cell membrane and multicellular filaments of marine gliding bacteria *Saprospira grandis* were used in this study. We selected multicellular filaments (10-100 unit bacterial cells) of a few marine *Saprospira* isolates, since the attachment signal of a single cell could be amplified.

Expanding mercury sphere electrode (dropping mercury electrode) is used as a probe. Its main advantage is: (i) an ease of varying surface charge and interfacial tension: (ii) the fluidity of the interface enhances adhesion of cells and is also typical of most marine interfaces.

Initial attachment and spreading of a single *Saprospira* filament that reaches the electrode/electrolyte interface results in a rapid (tens of milliseconds) current transient caused by the displacement of ions and water molecules from the contact area of the interface. Amplitude and duration of each attachment signal reflect both size and interfacial reactivity of the filament. Signals were strain and growth condition specific. Oscillatory attachment signals were observed in some cases. The attachment is confined to a broad range of positive and negative charges of the electrode surface (from +19.7 to -10.6  $\mu\text{C}/\text{cm}^2$ ) and it depends critically on the interfacial tension. Hydrophobic interaction could be considered as a major driving force in adhesion of *Saprospira* filaments at the charged mercury interface.

## 655.F1 ROLE OF ELECTRICAL AND MECHANICAL PROPERTIES OF RED BLOOD CELLS FOR THEIR AGGREGATION

S. Jovtchev<sup>1</sup>, I. Dzhenev<sup>1</sup>, S. Stoeff<sup>1</sup> and S. Stoylov<sup>2</sup>

<sup>1</sup>Dept. of Physics and Biophysics, Medical University - Sofia, 1431 Sofia, Bulgaria

<sup>2</sup>Inst. of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

The behaviour of red blood cells (RBC) in flow is dependent on the processes of aggregation-disaggregation, orientation and deformation. The complex individual cellular properties concerning these processes are mainly the aggregability and the deformability. The aggregability of RBC is predominantly determined by the glycocalyx on their membranes, in particular by the amount of the sialic acid residues bearing negative surface charge and their distribution, by their form and by their deformability. The deformability of RBC basically depends on the mechanical and electrical properties of their membranes, on their form and on their cytoplasmic viscosity.

In previous investigations using a novel electro-optical technique we found that RBC orientation and disorientation in alternating electric field (1 kHz) is influenced by their deformability [1], conformational state of their glycocalyx [2] and by the concentration and properties of neutral macromolecules (dextran and

polyethylene glycol) in the suspending medium [3]. This makes the suggested electro-optical method useful for studies concerning the aggregability and deformability of RBC.

In the present investigation we have altered the surface charge density of the RBC by treatment with sialidase and their deformability by fixing them with glutaraldehyde. The electrical properties of RBC were estimated by means of cell electro-optics, cell electrophoresis and biochemical analysis of sialic acid content of their membranes. The deformability of the cells was determined by means of sedimentation technique and cell electro-optics. Additionally we observed the aggregation behaviour of the RBC in phosphate buffered saline, containing dextrin 70 000 as aggregating macromolecules and in autologous plasma using the zeta sedimentation technique [4].

The relationship between electrical polarizability, electrophoretic mobility and membrane sialic acid content, as well as their role and the role of cell deformability for the aggregation of RBC is discussed. Since RBC aggregation is very important for affecting blood viscosity at low shear rates and further relates to the sludging in the microcirculation, the possibilities which offers the electro-optical technique in studying RBC aggregability and deformability may be very useful for clinical practice, for testing pharmacological agents and for model investigations.

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## 656.F1 POINT OF MINIMUM CHARGE OF ELECTRODES IN SURFACTANT SOLUTIONS DETERMINED BY THIN LIQUID FILMS INVESTIGATIONS

M.K. Kaisheva<sup>1</sup> and Jean-Pierre Celis<sup>2</sup>

<sup>1</sup>Department of Physical Chemistry, University of Sofia, Sofia 1126, Bulgaria

<sup>2</sup>Catholic University of Leuven, Department of Metallurgy and Materials Engineering,  
B 3001 Leuven, Belgium

The formation of thin liquid films on a polarized electrode substrate from aq. solutions of colloid surface active agents is of significant interest in connection with many practical applications. Such is for example the understanding of the basic phenomena influencing the codeposition process, since the latter is connected with thinning and rupture of liquid films, formed between the electrode and the mineral particle at the moment of its arrival at the cathode as well as between hydrogen bubbles and electrode during hydrogen evolution.

A basic question exists connected with the codeposition of particles from aqueous plating baths. At the moment of its arrival at the cathode, a particle must stick to the electrode and be incorporated in the lattice of the metal, otherwise no composite coating can be formed. The investigation of the surface forces, acting between the particle and the electrode, not allowing the detachment of the particle, is closely connected with the possibility for obtaining higher quality deposits. These surface forces strongly depend on the sign and magnitude of the electrode charge, and for that reason the potential of zero or minimum charge of the electrode is an important characteristics necessary for the determination of the optimum electrodeposition conditions. Most precise methods for measuring the electrode potential of zero charge are based on differential capacitance investigations. These methods fail, however, when a surfactant is present in solution.

In this work the potential of minimum charge of a nickel electrode has been determined by investigating thin liquid films, formed between the electrode and an air bubble from aqueous solutions of sodium sulfate with the addition of the nonionic surfactant triethyleneglycol monolauryl ether (BRIJ30).

The microinterferometric method and the dynamic method have been used for the investigation of the thin liquid films. The dependence of the film thickness on time has been obtained, on the basis of which the isotherms of the disjoining pressure in the thin films have been found for different electrode potentials.

## 657.F1 INVESTIGATION OF THE CODEPOSITION OF SILICON CARBIDE POWDERS WITH NICKEL

M.K. Kaisheva<sup>1</sup>, J.P. Celis<sup>2</sup>, N. Muleshkov<sup>3</sup>, T. Muleshkov<sup>3</sup>, P. Nowak<sup>4</sup>,  
C. Dedeloudis<sup>2</sup> and L. Terziev<sup>1</sup>

<sup>1</sup>Faculty of Chemistry, University of Sofia, Sofia 1126, Bulgaria

<sup>2</sup>Catholic University of Leuven, Dept. of Metallurgy and Materials Engineering, B 3001 Leuven, Belgium

<sup>3</sup>Coroza Engineering, Sofia 1126, Bulgaria

<sup>4</sup>Polish Academy of Sciences, Institute of Catalysis and Surface Chemistry, Krakow, Poland

The introduction of small particles suspended in an electrolytic plating bath into a deposited layer on the surface of an electrode during metal electrodeposition is called composite plating. Depending on the type of particles, the simultaneous deposition of particles and metal ions leads to specific unique properties of the produced coating layers. The electrochemical synthesis of composite coatings is intensively studied recently with the purpose of creating the basis of advanced technologies for the production of surfaces with protective, wear resistant, corrosion resistant and other specific properties. Composite coatings like Ni-SiC are introduced successfully in automotive industry. The first development was the production of nickel-silicon carbide wear resistant coatings in the Wankel motor. Another application of nickel-silicon carbide coatings is as cylinder lining in aluminium engines. The control of plating conditions however during the process of codeposition is very important for the reproducibility of the quantity of the codeposited particles and the uniformity of their distribution. In the present work codeposition of nickel with silicon carbide powders from different origins has been investigated. The dependence of the weight percentage of SiC in the coating has been studied as a function of the suspension concentration. Scanning electron micrograms of the coatings and of their cross-sections have been taken. Microhardness of the coatings has been studied as a function of the percentage of incorporated SiC. The increase in the SiC concentration leads to an increase in the microhardness of the Ni-SiC composite coating. Friction coefficients of the coatings have been determined as well.

## 658.F1 HOW TO HANDLE THE ION ADSORPTION DATA WITH VARIABLE SOLID-TO- LIQUID RATIOS BY MEANS OF FITEQL

Marek Kosmulski

Forschungszentrum Karlsruhe GmbH, Institut für Nukleare Entsorgungstechnik,  
Postfach, 3640, 76021 Karlsruhe, Germany

FITEQL requires a constant solid-to-liquid ratio in serial data for calculations involving different models of electric double layer. Two dummy-components introduced in the present paper make it possible to handle data with variable solid-to-liquid ratios without changing anything in the source code. Experimental data (nickel and gadolinium adsorption on alumina) obtained for solid-to-liquid ratios ranging from 2 to 200g (300 to 30 000 m<sup>2</sup>) per liter are analyzed as an example.

## 659.F1 IS THERE ANY UNIVERSAL SOLVENT SCALE TO PREDICT THE SOLVENT EFFECTS ON THE SURFACE CHARGE DENSITY OF VARIOUS OXIDES?

Marek Kosmulski and Andrzej Plak

Polish Academy of Sciences, Institute of Catalysis and Physical Chemistry of Interfaces,  
ul. Niezapominajek, 30-239 Krakow, Poland

Many organic cosolvents cause a decrease of negative surface charge of oxides in mixed solvents as compared with purely aqueous systems. The extent of this effect depends on the nature of the organic cosolvents. The magnitude of the surface charge density of a given oxide in mixed solvents may be used to build a special solvent scale. Correlation of such solvent scales built for silica, alumina and titania and interrelations between these solvent scales and well known solvent scales based on solvatochromism and NMR shifts are studied.

## 660.F1 USE OF OPTICAL FORCES TO DETACH SINGLE MICROSCOPIC PARTICLES ADHERING TO FLAT SURFACES IN AQUEOUS MEDIA

R.B. Liebert, D.L. Desrosiers and D.C. Prieve  
*Carnegie Mellon University, Pittsburgh, USA*

Photons of light can be considered as particles possessing momentum which is proportional to their energy. The proportionality constant is the reciprocal of the speed of light, or about 4.5 nN/W in air. Any change in momentum of the photons owing to their encounter with an object (e.g. reflection, scattering) exerts a force on the object whose magnitude and direction is determined by conservation of momentum. We used Total Internal Reflection Microscopy to measure the optical force exerted on 10  $\mu\text{m}$  polystyrene spheres immersed in water when a few milliwatts of light energy (514.5 nm) was focused to a waist diameter comparable to the diameter of the sphere. Near the waist the optical force was measured as 0.34 nN/W which is within experimental error of that predicted using ray optics.

Having characterized the optical force on levitated microspheres using a low-power laser, we attempted to detach 10  $\mu\text{m}$  polystyrene or glass spheres adhering to a glass microscope slide immersed in water using a higher power beam, oriented normal to the slide. Apparently identical spheres exhibited widely different adhesion strengths. Separately testing individual particles from an ensemble of 40 to 50 stuck spheres, a few percent of the spheres could be detached by optical forces as low as 10 pN, whereas nearly 100 pN was required to detach nearly all spheres. Owing to very low absorption of visible light by polystyrene, the steady state temperature rise by a sphere was estimated to be less than 0.01  $^{\circ}\text{C}$  at the highest power level used.

## 661.F1 UNDERSTANDING THE STAGNANT LAYER PROPERTIES IN ELECTROKINETICS

J. Lyklema<sup>1</sup>, M. Minor<sup>1</sup>, S. Rovillard<sup>2</sup>, J. de Coninck<sup>2</sup>

<sup>1</sup>*Wageningen Agricultural University, Department of Physical and Colloid Chemistry,  
Dreijenplein 6, 6703 HB Wageningen, The Netherlands*

<sup>2</sup>*Centre de Recherche en Modélisation Moléculaire, 20 Place du Parc, 7000 Mons, Belgium*

All electrokinetic phenomena involve tangential transport of liquid with respect to a charged surface, or conversely. General experience has shown that upon this motion a thin layer of liquid remains adhered to the solid: the stagnant layer. It is generally assumed that there is a sharp transition between the stagnant layer and the bulk liquid, the slip plane. The electrokinetic or  $\zeta$ -potential is identified as the potential at the slip plane.

So far the properties of the stagnant layer or, for that matter, the mechanism of the slip process, has remained enigmatic. Nevertheless these properties are of great relevance because the stagnant layer connects the surface properties of a colloid to its electrokinetic characteristics. The former can be obtained by, say, titration but the latter determines interaction and rheology.

Using dielectric relaxation and other electrokinetic techniques we have now obtained more insight into the macroscopic properties of the stagnant layer. These properties have now also received a molecular interpretation through Molecular Dynamics simulation.

Macroscopically speaking, the stagnant layer behaves as a two-dimensional gel. The water in it is immobilized, but nevertheless the self-diffusion coefficient of water, and the tangential mobilities of ions in that layer, are not significantly lower than in the bulk phase. Stagnant layers occur both on hydrophilic as on hydrophobic surfaces, hence the interaction between water molecules and the surface cannot be the reason for its existence. Rather the water-water interaction is determinative.

Molecular dynamic modelling has now proven that the apparent macroscopic stagnancy and the relatively high mobility on a molecular scale are fully compatible. A poster by Rovillard, Lyklema and De Coninck gives details.

## 662.F1

THE PROCESSES THAT ACCOMPANY ELECTROKINETIC  
PHENOMENA OF THE SECOND KIND

Natalia Mishchuk

*Institute of Colloid and Water Chemistry, the Ukrainian Academy of Sciences,  
pr. Vernadskogo, 42, Kiev, 252680, Ukraine*

Electroosmosis and electrophoresis of the second kind were predicted a few years ago. Now these phenomena are investigated for different types of particles and fibres: ion-exchanger, metal, carbon, semiconductor. These new electrokinetic phenomena are due to the essential decrease of electrolyte concentration near the particle surface and the appearance of induced space charge behind the quasi-equilibrium electrical double layer. It was shown, both theoretically and experimentally, that the velocities of electroosmosis and electrophoresis of the second kind are by one or two orders of magnitude higher than those calculated on the base of Smoluchowsky theory. However, there are a few different factors which act on the induced space charge and can change the main characteristics of the electrokinetic phenomena mentioned.

The local warming and growth of temperature in the region of low electrolyte concentration may be one of them. Thus the possibility of two heat effects exist: local increase of the diffusion coefficient and the thermoconvection. Both these effects can essentially change the characteristics of the concentration polarization in the case of flat interface, but they are insufficient for curved particle surface.

Another factor that can change the characteristics of electrokinetic phenomena is the dissociation of the water. The polarization process leads to the local electrolyte concentration decrease to  $10^{-7} \text{ eq l}^{-1}$ . Thus the concentration of electrolyte in this region reaches a value corresponding to the local equilibrium of the water dissociation reaction ( $C_H C_{OH} = 10^{-14} \text{ eq}^2 \text{ l}^{-2}$ ). As a result,  $H^+$  and  $OH^-$  ions cause an electrical conductivity increase in the region of induced spacecharge and reduce the space charge and the velocity of electroosmosis and electrophoresis. Original method of experimental investigation of the water dissociation near a particle surface is proposed.

Theory of the electrokinetic phenomena of the second kind was developed with the approximation of thin double layer and thin region of induced space charge. Simultaneously we supposed that the tangential flux of ions is absent. However, the role of tangential processes increases in strong electric fields. One of the main factor which reduces the velocity of electroosmosis and electrophoresis of the second kind is tangential drift of induced space charge connected with the very high velocity of liquid near the particle surface.

The main condition for the existence of new electrokinetic phenomena is low conductivity of electrolyte. But in special cases the particle conductivity can depend on the electrolyte concentration. The theoretical model for the velocity diminution with the change of particle conductivity is developed.

All results of the theoretical study of the processes which accompany the electrokinetic phenomena of the second kind are in good agreement with the experimental data.

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## 663.F1

ELECTROKINETIC PHENOMENA IN WIDE-POROUS MEMBRANES  
AT THE REGIME OF OSCILLATING PRESSURE

Natalia Mishchuk

*Institute of Colloid and Water Chemistry, the Ukrainian Academy of Sciences,  
pr. Vernadskogo, 42, Kiev, 252680, Ukraine*

Usually the investigations of streaming current or potential are carried out with using of constant pressure drop on the membrane. But there is a principle possibility to extend the receiving information about investigated systems by using the periodical regime, for example, oscillating pressure. This regime is interesting not only for scientific study, but also have the essential importance for the creation of device, which exchange the energy of the pressure and the hydrodynamic flow with the special time configuration into the current or potential signal.



The theory of streaming current and potential through the membrane with wide cylindrical capillaries is developed for the pressure with sinusoidal characteristic. Taking into account that each compound function may be presented as sum of sinusoidal functions, our theoretical model may be also used for the description of more complicated impulses of pressure.

The analytical expressions for the time dependence of concentration distribution in the membrane porous and near the membrane surfaces are received for two limiting cases: low and high frequencies. We take into account the hydrodynamics transport of ions, electromigration and diffusion ion flux and the peculiarities of hydrodynamic flow in periodical regime which in high frequency case essentially distinguish from the flow with the stationary profiles. Also we analyze the electroviscous effect, the role of the difference between the Stern potential and the electrokinetic one and the displacement of the phase relatively to the phase of using oscillating pressure. The approximation of small Peclet numbers is used.

The peculiarities of concentration polarization in presence of some resistance  $R$  included in the electrical circuit, are investigated ( $R = 0$  corresponds to the regime of streaming current,  $R = \infty$  corresponds to regime of streaming potential). The resistance changes not only amplitude of streaming current or potential phase, but also leads to the additional displacement of the phase.

The role of conditions of experimental investigations are discussed. It is shown that the electrode polarization may essentially change the results of measurements. The possibilities of insufficient influence of electrodes are analyzed.

## 664.F1 NANOPARTICLES AND THEIR APPLICATION IN MeH- BATTERIES

M. Mitov<sup>1</sup>, A. Popov<sup>2</sup> and I. Dragieva<sup>2</sup>

<sup>1</sup>South-West University, Blagoevgrad, Bulgaria

<sup>2</sup>Central Laboratory of Electrochemical Power Sources,  
Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

One of the recent applications of nanoparticles obtained by borohydride reduction is their use as a basic functional component in the so called metal-hydride electrode. The results presented in this report demonstrate the dependence of the properties of such nanoparticles on the presence of hydrogen and boron in them. The quantities of hydrogen and boron were varied by the conditions in which the reduction process in salt aqueous solutions was performed. XPS investigation data on the surface composition of the as prepared amorphous and crystalline nanoparticles as well as data for this composition change resulting from the electrochemical charge-discharge cycling have been presented.

Electrodes of a simple model composition, obtained at various press densities and sinter temperature were subjected to cycle-life tests. The results have been used to characterize the electrochemical behaviour of the electrode material. An hypothesis has been proposed for the mechanism of the action of metal-hydride electrodes prepared with such a type of nanoparticles.

## 665.F1 THE DISPERSION OF THE ELECTROPHORETIC MOBILITY OF THREE INFLUENZA VIRUS STRAINS

L.M. Molodkina<sup>1</sup>, E.V. Golikova<sup>2</sup>, V.M. Molodkin<sup>1</sup>, Yu.M. Chernoberezhsky<sup>3</sup>

<sup>1</sup>St. Petersburg State Technical University, St. Petersburg, Russia

<sup>2</sup>The State Optical Institute named by S.L. Vavilov, St. Petersburg, Russia

<sup>3</sup>The Technological University for Plant Polymers, St. Petersburg, Russia

It is known that the knowledge of the variation of particles electrophoretic mobility allows to estimate the heterogeneity extent of the interface and is very important for the disperse systems aggregative stability investigations. The electrokinetic properties of influenza virus particles of three strain have been investigated by a microelectrophoretic method in the wide range of pH and concentration of NaCl, NaNO<sub>3</sub>, CaCl<sub>2</sub> and BaCl<sub>2</sub> electrolytes. The field of the microscope was illuminated by a laser beam focused to a diameter of 30  $\mu\text{m}$ . The mobility of 30-80 particles was determined in each experiment. The statistic treatment of experimental data was made for the obtaining the dependences of root-mean square deflection electrophoretic mobility of virus particles ( $\sigma$ ) and the variation factor of the mobility ( $C_v = \sigma/U$ ) on pH of medium, on the electrolyte concentration, on time and so on. The correlation of these dependences with the

dependences of modulus of mean electrophoretic mobility ( $|U|$ ) on the same parameters had been obtained. Thus we have presented the experimental results as the dependences of  $\sigma$ - $|U|$  and  $C_v$ - $|U|$ . The dependences obtained for all studied influenza virus strain (A/Leningrad/54/1, A/Kiev/ 59/79 and A/Chile/1-/83R<sub>2</sub>) and electrolytes have shown that increasing of the  $|U|$  was by an increase in  $\sigma$ . The sets values of  $\sigma$  are within the zone, that width and tangent of the declivity angle are different for each strain. The type of  $C_v$ - $|U|$  dependence was determined for all the investigated strains.

These data permit to conclude that the dependence  $\sigma$ - $|U|$  and  $C_v$ - $|U|$  may serve as the characteristics of electrosurface properties of individual influenza virus strain.

## 666.F1 QUANTUM OSCILLATIONS OF A SOLVATED ELECTRONS NEAR INTERFACE SEPARATING INSULATING PHASES IN SQUEEZING ELECTRIC AND EXTERNAL MAGNETIC FIELDS

V.K. Mukhomorov

*Agrophysical Institute, 14 Grazhdansky, St. Petersburg, 195220, Russia*

It is well known that electrostatic image forces act on a charge in homogeneous isotropic dielectric medium in the vicinity of a planar interface with another dielectric medium. Applying a uniform squeezing electric field perpendicular ( $z$  axes) to the interface plane, we can compensate the electrostatic image forces and, therefore localize the charge at some equilibrium distance from the interface. This paper analyzes the oscillations of a solvated electron about its equilibrium position and also the interaction between electrons with allowance for the effect of a uniform magnetic field parallel to an applied electric field.

The conditions are identical under which the electrostatic image forces at an interface between the insulating phases result in spatial confinement of a solvated electron. The Bogolyabov-Tyablikov method of collective coordinates is used to derive equations describing oscillations of the center of inertia of electron near its equilibrium position. It is shown that motion of a solvated electron in the vicinity of an interface separating dielectric phases subjected to external fields is completely quantized: it is quantized by the squeezing electric field in the direction of the  $z$  axis and by the magnetic field in the plane parallel to the interface. It is found of the upper and lower limits on the fields and temperature in which the electron oscillations are not suppressed. In Ref 1,2 the oscillations energy spectrum of the electron near interface was found in the harmonic approximation. A longrange resonant interaction of two oscillators resulting in the appearance of effective attraction between electrons is discussed. In Ref.3 it is shown that the repulsive barrier between solvated electrons has a finite value. We discuss the possibility of a lowering of the potential barrier and hence of an effective shift of the dynamic equilibrium between solvated electrons and coupling two-electron formations (bipolarons) in the direction of electron pairing. The interelectron potential at large distance is determined by its Coulomb asymptotic behavior and has a maximum at 12 Å and minimum at 3.5 Å [4]. Numerical estimates are obtained for a specific case of the electron states in ammonia.

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## 667.F1 AB-INITIO HARTREE-FOCK STUDY OF BRØNSTED ACIDITY AT THE SURFACE OF OXIDES

P. Nortier<sup>1</sup> and M. Allavena<sup>2</sup>

<sup>1</sup>*Service de Synthèse Minérale Rhône-Poulenc Recherches, 52 rue de la Haie-Coq  
93308, Aubervilliers Cedex, France*

<sup>2</sup>*Laboratoire de Chimie Théorique (UPR 9070 CNRS), Université Pierre et Marie Curie,  
4 Place Jussieu, 75252 Paris Cedex 05, France*

Ab initio calculations using small sets of basis functions and pseudo potentials within the framework of the cluster model have been applied to the determination of a scale of acidity at oxide surfaces. Results are compared with available experimental data and correlated to values deduced from electrostatic models as

MUSIC. A fair agreement between the series of data supports the validity of local models for evaluating acidic properties on oxides surfaces. The acidity of the surface sites of oxides is driven by the electrostatics of the system and is mainly governed by the structural parameters: the acidity increases with the coordination number of the hydroxyl group and the charge on the cation(s), and decreases when the coordination number of the cation(s) increases.

## **668.F1 THE INFLUENCE OF INERT PARTICLES SUSPENDED IN SOLUTION ON THE PROCESS OF ELECTROCRYSTALLIZATION OF METALS - AN ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY STUDY**

**Pawel Nowak<sup>1</sup>, Robert Socha<sup>1</sup>, Milliana Kaisheva<sup>2</sup>, Jean-Pierre Celis<sup>3</sup> and Zdravko Stoinov<sup>4</sup>**

<sup>1</sup>*Polish Academy of Sciences, Institute of Catalysis and Surface Chemistry, Krakow, Poland*

<sup>2</sup>*University of Sofia, Department of Physical Chemistry, Sofia, Bulgaria*

<sup>3</sup>*Katholieke Universiteit, MTM, Leuven, Belgium*

<sup>4</sup>*Bulgarian Academy of Sciences, Institute for Electric Power Sources, Bulgaria*

The codeposition of inert particles suspended in the plating bath during electrocrystallization may be an unwanted phenomenon, leading to contamination of the obtained metal. On the other hand this phenomenon is the basis of the important technological process -codeposition of composite coatings.

The influence of the particles of several metal oxides and carbides suspended in solution on the electrocrystallization of nickel and copper was investigated by impedance spectroscopy. If particles are not included into the growing metal layer, their presence in suspension does not influence the impedance characteristics of the electrode, except in the case of the extremely fine particles.

If particles are embedded into the growing metal layer, the impedance parameters of the process of electrodeposition (Faradaic reaction resistance, double layer capacitance) change, and these changes are more pronounced the higher the concentrations of particles incorporated in the metal. At the same time inhomogeneity of the electrode increases, which may be inferred from the more pronounced frequency dispersion of the impedance parameters.

The influence of some surfactants on the process of metal electrodeposition in particle suspensions was investigated as well. Strong retardation of the electrodeposition process was observed in the case of several surfactants.

## **669.F1 HETEROGENEOUS HYDROLYSIS AS A VARIETY OF HETEROGENEOUS REACTIONS IN THE OXYHYDROXIDES SUSPENSIONS**

**S.I. Pechenyuk**

*Kola Science Centre of RAS, Institute of Chemistry, Apatity, Russia*

A variety of heterogeneous reactions of complex compounds in the crystalline and (or) amorphous oxyhydroxide suspensions is described. It is explained as a sorptional-hydrolytic decomposition of complex compounds in a dispersed system on the interface between the electrolyte aqueous solution and the oxyhydroxide surface. This process occurs by the ligands detachment from the inner sphere at a rate equal to that of transition of the complex central ion (C.I.) from the dispersion medium bulk onto the dispersion phase oxyhydroxide surface. This phenomenon is accompanied by the formation a new amorphous phase of the C.I. hydroxide on the first amorphous phase surface. In this process all the initial components of the system, i.e. the complex, the oxyhydroxide, the electrolyte of the medium and the water participate. The kinetic investigations were carried out on the examples of platinum metals, copper, chromium and mercury acidocomplexes in the suspensions of iron (III), rare earth elements (REE), titanium and zirconium (IV), chromium and indium (III) amorphous and crystalline oxyhydroxides. The role of such factors as the nature of the complex, the system temperature, the dispersed phase basicity, the specific surface area, the nature and concentration of the ionic media, both the complex and sorbent concentration was studied. The nature and magnitude of the ionic medium effect on the process rate was explained by establishing the electrolyte

macrocomponent participation mechanism in the intermediate. The main peculiarity of the heterogeneous hydrolysis consists in that the sorbat is not fixed by the sorbent in the initial form. The process occurs by the ligands substitution for the water molecules in the complex located on the dispersed phase surface for a short time.

## **670.F1 INTERACTIONS BETWEEN INORGANIC COLLOIDAL SILICAS AND SEMI-CERAMIC ULTRAFILTRATION MEMBRANES**

**B. Putman and P. Van der Meeren**

*University of Ghent, Faculty Agricultural and Applied Biological Sciences,  
Department of Applied Analytical and Physical Chemistry,  
Laboratory of Applied Physical Chemistry, Coupure Links 653, B-9000 Gent, Belgium*

The influence of the charge density of inorganic particles on the ultrafiltration permeate flux was already investigated several years ago. As the membrane also bears charges, interactions between the charged particles and the charged membrane might affect the permeate flux too.

This hypothesis was investigated with the ultrafiltration of different types of commercially available colloidal silicas of different iso-electric points (Ludox®) on several semi-ceramic membranes containing different metal-oxides. For both the membrane and the silicas, the zeta-potential was investigated as a function of pH. For the characterisation of the state of ionisation of the membrane, streaming potential measurements were used whereas potentiometric titrations were applied to characterise the particle charge density.

Subsequently the interaction between both components was investigated by measuring the streaming potential of the membrane when Ludox® was added. From the measurements of oppositely charged membrane and silica, it could be seen whether the Ludox® only neutralises the charge of the membrane or adsorbs to the membrane and forces its own charge to the membrane. In addition, the reversibility of the interaction was investigated.

Through combination of the different membranes and Ludox® types at different pH values, it was possible to determine the influence of the membrane-particle and the particle-particle interactions on permeate flux in cross-flow ultrafiltration.

## **671.F1 THE DYNAMIC MOBILITY AND DIELECTRIC RESPONSE OF NA-BENTONITE**

**Mikael Rasmusson<sup>2</sup>, William Rowlands<sup>1</sup>, Richard W. O'Brien<sup>1</sup> and Robert J. Hunter<sup>1</sup>**

*<sup>1</sup>School of Chemistry, University of Sydney, NSW 2006 Australia*

*<sup>2</sup>Department of Physical Chemistry; University of Göteborg and Chalmers University of Technology,  
S-412 96 Göteborg, Sweden*

Bentonite is a common clay, used in many industrial processes, such as paper making and mudd drilling. It has been found that the degree of stacking of unit layers in an individual sodium bentonite particle decreases with decreasing clay concentration. However, there is no complete dissociation into single unit layers despite the highly developed electrical double-layer which one would expect from the relatively high surface charge density. A new electroacoustic instrument (AcoustoSizer, Matec Applied Sciences) has been used to measure the dynamic mobility of relatively concentrated (1-2%) Na-bentonite suspensions. Information about the particle size distribution and the  $\zeta$ -potential can be obtained from the dynamic mobility spectrum. For bentonite particles, the interpretation of the dynamic mobility spectrum is complicated by the presence of anomalously high surface conductance. The surface conductance of the particles can be determined directly by dielectric response measurement on a high-frequency conductance bridge. The surface conductances determined in this way agrees very well with those needed to fit the dynamic mobility spectrum.

## 672.F1 MODELING OF 2D FIRST-ORDER EQUILIBRIUM PHASE TRANSITIONS IN ANODIC MONOLAYERS USING THE ISING LATTICE GAS MODEL

U. Retter and W. Kant

*Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany*

Charge density-potential isotherms with 2D first-order phase transitions are considered for anodic monolayers at the metal/electrolyte interface. Using the Ising lattice gas model, theoretical charge density-potential isotherms have been derived for the triangular, the square and the honeycomb lattice. For various temperatures, the experimental charge density-potential isotherms of HgS monolayers at the mercury/electrolyte interface can be theoretically well described with the Ising lattice gas model. As result, the lateral interaction energy and the adsorption energy of the HgS monolayer molecules have been determined. Till now, these two characteristic quantities have not been known for anodic layers.

## 673.F1 ON TWO NEW DISSOLUTION MECHANISMS OF ANODIC LAYERS

U. Retter and W. Kant

*Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany*

Two models have been derived concernig the dissolution of anodic layers at the metal/electrolyte interface. The first model involves an electrodesorption of a two-phase adsorbate. Here, adclusters of a condensed phase dissolve at their rims into admolecules of an expanded phase and only the admolecules can be electrodesorbed. The electrodesorption is assumed to be much slower than the dissolution of the adclusters. When all adclusters are dissolved, the electrodesorption of the admolecules follows a first-order process.

The second model refers to a reverse 2D nucleation-growth-collision. Here, the dissolution of 2D islands at their rims is rate determining. This mechanism differs markedly from a 2D hole-nucleation-growth-collision.

The two new dissolution mechanisms have been verified for HgS monolayers at the mercury/electrolyte interface.

## 674.F1 ELECTROKINETICS: MOLECULAR INTERPRETATION OF STAGNANT LAYER PROPERTIES

S. Rovillard<sup>1</sup>, J. Lyklema<sup>2</sup>, J. De Coninck<sup>1</sup>

<sup>1</sup>*Université de Mons-Hainaut, Centre de Recherche en Modélisation Moléculaire  
20, Place du Parc, 7000 Mons, Belgium*

<sup>2</sup>*Wageningen Agricultural University, Dept. of Physical and Colloid Chemistry,  
Dreijenplein 6, 6703 HB Wageningen, The Netherlands*

General experience stemming from electrophoresis, electro-osmosis and other electrokinetic phenomena has shown that only a fraction of the countercharge of electrical double layers is accessible. The difference between the electrokinetically measurable surface charge density and the surface charge density is usually attributed to the presence of a stagnant layer.

According to present-day insight the stagnant layer behaves as a two-dimensional gel in that its viscosity is very high (in fact, in the current models it is infinitely high), but that the tangential mobilities of counterions embedded in it is very close to the corresponding values in bulk.

Our aim is to understand at a microscopic level, the behavior of such systems, using molecular dynamic simulations.

With computer simulations, it is possible to follow the trajectories of the different types of particles with no induced perturbations. Dividing the system in several layers (at the atomic scale) emphasizes the evolution of its properties by studying the system from the surface of the surface to the bulk.

The proposed poster will be focused on the MD tool to understand how specific properties in the ions and solvent trajectories can influence the macroscopic properties of the system.

## 675.F1 THE CONTACT POTENTIAL DIFFERENCE AND INTERACTION OF METAL SURFACES AT MICROSCOPIC GAP BETWEEN THEM

L.A.Rudnitsky

*Institute for Nitrogen Industry, Zemlyanoi val 50, 109815 Moscow, Russia*

The effect of the cpd (contact potential difference) between metal planes separated by a gap was described many years ago. However, when the gap size ( $L$ ) diminishes to atoms size order, the problem of cpd is not so clear. In this case, the charge transfer between the planes, which accompanies the cpd creation, may increase up to values which are comparable to value of the charge transfer between metal support and adatoms or adions submonolayer. This induces the change of the surface potential jumps ( $\sigma_j$ ) over the planes adlayers, attended with variation of cpd, and distortion of adions potential curve.

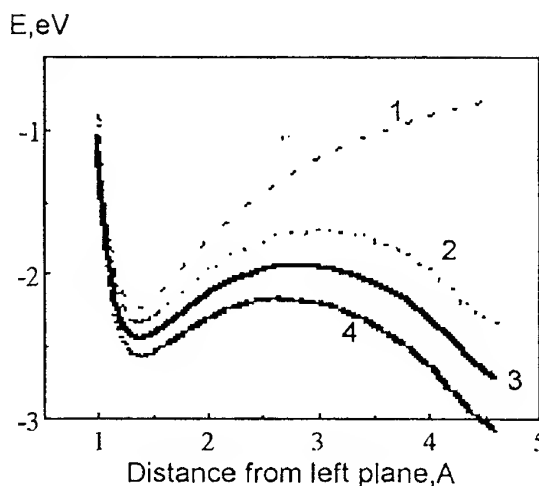
The simple model (one of the identical metal planes is covered by adions) has been described based on the electrostatic principle of division of the charge, which compensates for the adsorbed ions charges.

The two limiting cases have been studied in this work: 1) The positive monocharged ions submonolayer adsorbed on one of two identical parallel planes. This system consisting of metal planes and submonolayer of adsorbed ions has been described as a model of two flat capacitors connected in parallel, where both planes potentials are equal to zero. It was found that the charge transfer between the planes induces cpd decrease. At the elected values of the parameters ( $r_i=1.35$  Å and  $L = 5$  Å), it can receive cpd decrease as much as 10%.

The potential energy  $E$  was calculated for the monocharged positive ion ( $r_i=1.35$  Å) inserted in the gap between two parallel planes.

$E$  was calculated as the sum of mirror images forces terms, repulsive terms and cpd contribution. The results of the calculations are given in the Fig. We can see the decrease of the desorption potential barriers heights at  $L$  decreasing and cpd increasing.

The mechanism of this phenomenon can be described as follows: in the beginning, the ion energy is determined by its interaction with the single mirror image on the left plane. The right plane approach gives rise to infinite quantity of the ion mirror images, the interaction energy with which can be described by two infinite convergence series - the "left" one and the "right" one. The sum of the additional terms of the "left" series is the positive value. The sum of the "right" series terms is the negative one. So the decrease of the ion attractive energy with the left plane and increase of the common attractive energy with both planes occurred. In this case the part of the negative charge moves from the left plane to the right one.



The dependencies of potential energy  $E$  of the ion on its distance from the left plane for varying cpd values.

The curve 1 corresponds to macroscopic values of  $L$ . The curves 2, 3 and 4 correspond to  $L=6$  Å and cpd values 0, 0.5 and 1 V respectively.

**676.F1****ZETA POTENTIOMETRY AS A TOOL FOR MEASURING  
THE ADSORPTION OF SURFACTANTS AT GAS/LIQUID INTERFACES****P. Saulnier<sup>1</sup>, F. Boury<sup>1</sup>, P. Bouriat<sup>2</sup>, J. Lachaise<sup>2</sup>, G. Morel<sup>2</sup>, A. Graciaa<sup>2</sup>**<sup>1</sup>*L. B. P., Faculte de Pharmacie, 49045 Angers, France*<sup>2</sup>*L.T.E.M.P.M., Centre Universitaire de Recherche Scientifique, 64000 Pau, France*

$\zeta$ -potentials of air bubbles immersed in aqueous surfactant solutions are measured by using the improved spinning tube electrophoremeter method. The solutions in which are immersed the bubbles are solutions of an anionic surfactant, solutions of a polydistributed nonionic surfactant or solutions of their mixtures. When the solution contains a single surfactant (the anionic or the nonionic),  $\zeta$ -potentials decrease regularly versus time toward limit values which depend on the surfactant concentration. These decreases reflect adsorption kinetics of the surfactant molecules at the bubble surface.

When the solution contains a mixture of the two surfactants the variation of the  $\zeta$ -potential versus time is no longer monotonous. This new behavior is attributed to the competitive adsorption of the two surfactants which is ruled by the differences between the concentrations of the surfactants in the solution and their critical micelle concentrations. The study of the variations of the  $\zeta$ -potential at equilibrium versus the surfactant concentration allows to measure the critical micelle concentrations of the two surfactants or of their mixtures. Thus it is possible to find again the micellization diagram of the surfactant mixture which had previously been determined by classical methods such as surface tension or conductivity measurements. The difference from the ideal adsorption of the two surfactants at the bubble surface is clearly shown for surfactant solutions the concentration of which is higher than the critical micelle concentrations of the two surfactants. In this case the variation of the  $\zeta$ -potential versus the relative composition of the surfactants in the mixture goes through an extremum which is linked with the surfactant interactions.

The results reported and discussed in the paper demonstrate that the improved spinning tube electrophoremeter is an useful tool for measuring the competitive adsorption of surfactants at the air/solution interface, the surfactant interfacial interactions and the mixed micellization diagram.

**677.F1****MOLECULAR DYNAMICS SIMULATION OF IONIC SOLUTIONS  
IN CONTACT WITH CRYSTAL SURFACES****Hiroyuki Shinto, Takashi Sakakibara and Ko Higashitani***Kyoto University, Chemical Engineering Department, Yoshida, Sakyo-ku, Kyoto 606-01, Japan*

No word may be necessary to explain the importance of the knowledge about *how* an ionic crystal forms itself in aqueous solutions, but no satisfactory information has been given for this phenomenon including whole sequence of processes such as association, nucleation, deposition and dissolution. In order to understand its complicated phenomenon at the molecular level, we have been performing a series of molecular dynamics (MD) simulations especially related to the formation process of NaCl crystal. Our system is relatively simple, but we believe that it is sufficient to get insight into the fundamental aspects of the formation mechanism of an ionic crystal in aqueous solutions.

In this study, we focused on the structural and dynamical properties of water and solvated sodium and chloride ions next to the different type of faces such as NaCl (001) and NaCl (011). The rectangular MD cell used here consists of 216 water molecules (or 214 water molecules, a sodium ion and chloride one) and a slab of 432 ions arranged in 12 (001) lattice planes or of 576 ions arranged in 24 (011) lattice ones. Water-water, ion-water and ion-ion interactions were represented by using SPC/E, Pettit-Rosky and Tosi-Fumi models, respectively. The usual periodic boundary conditions were applied. The calculations reported here were carried out over 10000 integration steps with  $\Delta t = 1.0$  fs at average temperature 298 K.

Conclusions from the results obtained in this study are summarized as follows; (1) More than two adsorbed-layers of water are strongly formed in the vicinity of NaCl (001) and (011) surfaces and the structures of these water layers are quite different. (2) Preferable configurations of solvated sodium and chloride ions near the surfaces are different and depend on the type of NaCl crystal surfaces. (3) No ion dissolving from the crystal into water can be seen during simulating time 10 ps, indicating that the ideal surfaces with no lattice defect such as NaCl (001) and (011) are stable in water at 298 K.

**678.F1 ELECTROKINETIC PHENOMENA AND SURFACE STRUCTURE****Frank Simon<sup>1</sup>, Stefan Spange<sup>2</sup>, Dieter Pleul<sup>1</sup> and Hans-Jörg Jacobasch<sup>1</sup>**<sup>1</sup>*Institute of Polymer Research Dresden, Hohe Str. 6, D-01069 Dresden, Germany*<sup>2</sup>*Dept. of Polymer Chemistry, University of Chemnitz, Str. der Nationen 62, D-09111, Chemnitz, Germany*

The observation of electrokinetic phenomena serves to describe thermodynamic properties of solid surfaces contacting liquid phases. An electrochemical double layer is formed between the solid and liquid phase. The structure of the electrochemical double layer is the result of the unknown solid surface properties and the well known properties of the used liquids. The zeta potential which may be calculated from streaming potential or electrophoretic mobility is a sensitive measure of the build-up of the electrochemical double layer. The dependence of the zeta potential on the pH and ionic strength of an aqueous electrolyte solution allows to calculate the adsorption potentials of the ions in the liquid phase and the surface charge density. On the other hand, the observed electrokinetic phenomena have to have molecular reasons. Thus, dissociation reactions observed in the electrokinetic experiment require functional dissociable surface groups and adsorption reactions of ions presuppose suitable adsorption centres on the investigated solid surface.

The aim of the presented paper is to show the relationship between molecular surface structure and electrokinetic behaviour. For this the surface structure and properties of silica powders have been changed by coating with polymer layers. X-ray photoelectron spectroscopy has been used to characterize the surface structure of the modified silica samples. The highly resolved C 1s and Si 2p spectra permitted to get information about the binding states of the carbon atoms in the surface region. The electrokinetic investigations were carried out by means of particle micro electrophoresis. From the results of the electrophoretic measurements in aqueous electrolyte solutions the Brønsted acid base properties of the solids have been evaluated. The relationships found between structure and properties allow a more general description of the surfaces of the investigated solids.

**679.F1 LOW-FREQUENCY DIPOLOPHORESIS OF THE PARTICLE WITH THE DOUBLE LAYER OF THE ARBITRARY THICKNESS****T. Simonova, V. Shilov, O. Shramko***Institute of Biocolloidal Chemistry, National Academy of Science of Ukraine, Kyiv, Ukraine*

Dipolophoresis of the second order on the field was described traditionally as the result of the nonuniform field action on the induced dipole moment of the particle. It is not enough for conductive media, but it is necessary to take into account also the field action on the polarization charges distributed in the liquid, because the force of this interaction is transmitted to the particle through the viscous tension. This new line of attack was began in the work by Shilov and Estrela-Lopis (1972) for the thin double layer. We represent the solution of problem for the arbitrary thickness double layer. Our consideration includes both linear and nonlinear on the external field polarization. The obtained results show for the case of the thin DL that the dipolophoretic velocity does not change by the change of the dipole moment sign. The traditional and electroosmotic components of the dipolophoretic velocity compensate each other in the case of the uncharged ideally polarizable particle. The forces acted on the charges of both the diffuse and diffusion layer are transmitted to a particle the less, the greater is DL thickness. We investigated the results for the different relationships among the polarizabilities of the particle and the medium.

**680.F1 NON-LINEAR ELECTROPHORESIS OF THE PARTICLE WITH THE DOUBLE LAYER OF THE ARBITRARY THICKNESS****T. Simonova, V. Shilov***Institute of Biocolloidal Chemistry, National Academy of Science of Ukraine, Kyiv, Ukraine*

The thin double layer (DL) approximation in the theory of the non-linear electrophoresis used by us previously (1976) is true in the water suspensions only. But non-water or water-organic media are more



preferable for the correct experimental investigations of the non-linear electrokinetic phenomena. For such media the DL thickness is less or comparable with the particle radius as a rule. These considerations have lead us to the problem of the DL non-linear polarization for media with the arbitrary electroconductivity. The results were obtained in the analytical form. This allows us to use the polarization characteristics for the description of the familiar and new effects of the strong field. In the weak field the DL polarization reveals in the electrophoretic mobility as the nonlinear on the Stern potential term. Contrary, the electrophoretic velocity of the third order with respect to an external field contains the linear on the equilibrium surface potential term. The solution of the Navie-Stocks equations gives us the general formula for the calculation of the spherical particle velocity for the axisymmetrical force distributed around the particle with the density:

$$\vec{f} = f_r(r) \cos \theta \cdot \vec{i}_r + f_\theta(r) \sin \theta \cdot \vec{i}_\theta \quad (1)$$

In (1)  $\theta$  - an angle between the radius  $r$  and the axis OZ. The velocity of the axisymmetrical motion of the particle is:

$$v = \frac{F_z}{6\pi\eta a} + \frac{1}{3\eta a} \int_a^\infty \left[ f_\theta \left( \frac{4}{3} r^2 - ar - \frac{a^3}{3r} \right) - f_r \left( \frac{2}{3} r^2 - ar + \frac{a^3}{3r} \right) \right] dr \quad (2)$$

$F_z$  is the force, acted immediately on the particle,  $\eta$  is the viscosity of the medium. Formula (2) is valid for the calculation of the velocity in an uniform electric field, in an nonuniform one and for the description of the nonelectrical force action. For the linear on the field electrophoresis in the case of the weakly charged particles formula (2) transforms to the Henry's formula.

## 681.F1

### ROTATION OF A DISPERSE PARTICLE WITH THE THIN DOUBLE LAYER IN A PERMANENT UNIFORM FIELD

T. Simonova, V. Shilov

*Institute of Biocolloidal Chemistry, National Academy of Science of Ukraine, Kyiv, Ukraine*

Theory of the stationary rotation of the uncharged bodies and particles in an permanent uniform field was developed by Simonova and Dukhin (1970-73). The angular velocity of the rotation is the linear function of the field  $E$  once  $E$  exceeds significantly the threshold  $E_0$ . The possibility of the rotation occurring spontaneously is determined by two conditions: 1) the mechanically non-stable orientation of the particle induced dipole moment (opposed to  $E$ ), 2) the sufficiently long time of the dipole relaxation. The dipole moment of the uncharged particle is opposed to an external field, but its relaxation time (the time of the Maxwell-Vagner polarization  $T_0$ ) is enough large in very low-conducting media only. This moment decreases with the increasing of the particle charge, goes through zero and takes the stable orientation. It seems that both the particle charge and the medium conductivity increasing are inconsistent with the conditions of rotation. But we took into account that the dipole moment of the charged particle fails into two parts. The greater one due to the fast Maxwell-Vagner polarization determines the sign of the whole dipole moment. The some less component of the moment with non-stable orientation is caused by the slow concentration polarization of the particle double layer (DL). Consequently, the DL polarization favours to the rotation of charged particles in conducting media. We have solved the problem of the rotated particle polarization in an permanent uniform field and have obtained the angular velocity as a function of  $E$ . For  $a=100$  mcm the threshold equals  $E_0=40$  V/cm if the Stern's potential of the thin DL is more than 50 mV.

## 682.F1

### UNDERPOTENTIAL DEPOSITION OF HYDROGEN ON PLATINUM INVESTIGATED BY DIFFERENTIAL IMPEDANCE SPECTROSCOPY

Z. Stoynov, D. Vladikova

*CLEPS -Bulgarian Academy of Sciences, 11 13 Sofia, Bulgaria*

The underpotential deposition of hydrogen on platinum in sulfuric acid was investigated by means of the impedance spectroscopy. The impedance measurements were carried out on Solartron 1174 Frequency Response Analyzer in the frequency range 10 KHz - 0,011 Hz with a density of 5 points per decade. The

Differential Impedance Analysis (DIA) was performed with the help of a Graphical Computer System Tektronix 4051. The nonstationary behavior of the system determined a special procedure for the electrode preparation and measurements. The form of the impedance diagrams was attributed to a modified adsorption model. The deviations from the ideal diagrams were explained with the surface inhomogeneity. An impedance time evolution was observed after reaching the working potential. The arc depression increases during the first 18 minutes, reaches its maximum and then decreases back to a new steady state condition. This change in the impedance behavior of the system could be explained with a process of "ORDER - DISORDER - ORDER". A more precise analysis of the impedance evidence for an UPD-adsorbate reorganization was obtained by DIA of the same impedance data. This new structural approach could distinguish the frequency ranges of different time constants and their distribution, which is an experimental evidence for the presence of different conglomerates on the surface with a cluster organization.

### 683.F1 ELECTRICAL DOUBLE LAYER AT $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> MIXED ELECTROLYTE (ETHANOL:AQUEOUS) INTERFACES

A. Sworska, J. Szczypa, W. Janusz,

*Department of Radiochemistry and Colloid Chemistry, M. Curie-Skłodowska University, Lublin, Poland*

The surface charge at the metal oxide/nonaqueous solvent originates from a dissociation of the surface groups of metal oxide and adsorption of ions from solutions. Mechanism of formation of surface charge, based on dissociation, depends on proton acceptor and proton donor properties of both: surface groups and of the solvent molecule properities (A. Kitahara, *Nonaqueous Systems in Electrical Phenomena at Interfaces* (A. Kitahara and A. Watanabe Eds), Surf. Ser, v.15, M. Dekker 1984, 119-143). Ethanol is poorly dissociated amphoteric solvent, with dissociation constant  $pK_{Ly} = 19.1$  and in universal scale in relation to water is shifted by - 4.2 units of pH. That means that at the same proton concentration the ethanol solution will be more acidic. Besides, mobilities of ions in ethanol solutions are lower, so the reaction kinetics should be slower (H. Galser, *pH Measurement*, VCH Weinheim 1991, 11.).

Hesleitner, N. Kallay, and E. Matijevic reported that the presence of ethanol, in the hematite/NaNO<sub>3</sub> solution system, has no influence on the surface charge density but decreases zeta potential (*Langmuir* 7, 1554-1555, 1991). They interpreted their experimental data as the evidence of ion association of the background electrolyte in the ethanol solution.

The main purpose of the present study was to investigate the adsorption of ions from the ethanol and mixed ethanol:water (1:1) solution of NaCl at hematite/electrolyte interface. The results of such measurements are compared with these for hematite/water solution system.

The presence of ethanol in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/NaCl solution system has no significant effect on the surface charge density vs pH relationship. However an influence of ethanol on zeta potential is greater and provokes the shift of iep from pH=8 in water solution to pH=9 in mixed ethanol:water (1:2). That has appeared as increase of the concentration of  $\equiv$ -SOH<sub>2</sub><sup>+</sup> groups in system with mixed ethanol:water solution. The adsorption of Cl<sup>-</sup> ions from ethanol:water solutions is greater and the adsorption of Na<sup>+</sup> ions is smaller than from water solutions. Ions adsorption data suggest that ion association cannot be responsible for adsorption behavior of hematite particles in mixed ethanol water solution. The ionization constants of surface groups are smaller in mixed solutions than in water ones so one can expect the increase of the concentration of positively charged groups and the decrease of concentration of negatively charged groups. This effect shifts iep towards alkaline region of pH scale. Similarly, the decrease of chloride complexation constant in mixed solution, in comparison to water, results in the increase of concentration  $\equiv$ SOH<sub>2</sub><sup>+</sup>Cl<sup>-</sup> groups. It agrees with higher adsorption of Cl<sup>-</sup> from ethanol:water than from water solutions. Complexation constants of Na<sup>+</sup> ions in ethanol:water and water solutions are comparable. However, the increase of the concentration of positive charged groups leads to the decrease of the concentration of  $\equiv$ SO<sup>-</sup>Na<sup>+</sup> groups in mixed solvent. Despite of lower mobility of ions in the ethanol solution the kinetic of adsorption of background electrolyte ions in the Fe<sub>2</sub>O<sub>3</sub>/ethanol solution of NaCl system is fast. The adsorption of Cl<sup>-</sup> from ethanol solutions is higher than from aqueous solutions, whereas adsorption of Na<sup>+</sup> is higher only for 0.1 mole\*dm<sup>-3</sup> of NaCl.

## 684.F1 PORE SIZE DEPENDENCY OF MEMBRANE CHARGE DENSITY OF CELLULOSE ACETATE-NITRATE MEMBRANE

Ryosuke Takagi<sup>1</sup>, Chieko Koretoh<sup>2</sup>, Keiko Gotoh<sup>3</sup>, Mieko Tagawa<sup>2</sup> and Masayuki Nakagaki<sup>4</sup>

<sup>1</sup>Shukugawa Gakuin Junior College, 6-58 Koshikiwa-cho, Nishinomiya 662, Japan

<sup>2</sup>Nara Women's University, Kita-uoya-higashimachi, Nara 630, Japan

<sup>3</sup>Kyoto University of Education, 1 Fukakusa-fujinomori-cho, Fushimi-ku, Kyoto 612, Japan

<sup>4</sup>Tokyo Inst. of Colloid Sci., 502 Higashi-Nakano 4-4-3, Tokyo 164, Japan

It is reported that the membrane charge density depends on pore size and electrolyte concentration in bulk solution. We have also reported that the membrane charge density of the Shirasu Porous Glass Membrane depends on its pore size. However, there are few papers that systematically treat the pore size dependency of the membrane charge density in a wide range of pore size. Then, in this paper, we study the pore size dependency of the membrane charge density in a wide range of pore size to make clearer the relation between the membrane charge density and the pore size. For this purpose, we used cellulose acetate-nitrate membranes (MF membranes) commercially delivered by Japan Millipore Ltd. The pore diameter of the membrane we used was 8.0, 1.2, 0.8, 0.65, 0.45, 0.22, 0.1 and 0.025  $\mu\text{m}$ . The membrane charge density was determined from the membrane potential measurement. The membrane potential was measured as a function of electrolyte concentration keeping the concentration ratio between bulk solutions to be two at 34°C. We used NaCl as an electrolyte. The membrane potential curves of the membranes of 0.8, 0.65, 0.45, 0.22, 0.1 and 0.025  $\mu\text{m}$  in pore diameter showed the S-shaped potential curves. On the other hand, the membrane potential of 8.0 and 1.2  $\mu\text{m}$  in pore diameter was constant and did not depend on the bulk concentration. The membrane potential was analyzed with the selective ion adsorption model in which the effect of ion adsorption was taken into account. As the results of analysis, it was found that the membranes of 8.0 and 1.2  $\mu\text{m}$  in pore diameter had no effective membrane charge and their membrane potentials were only the diffusion potential within the membrane. For other membranes, each membrane itself had also no fixed charge and the effective membrane charge was determined by the  $\text{Cl}^-$  ions adsorbed selectively on the pore wall. The adsorption coefficient did not depend on the pore diameter. Except the membrane of 0.025  $\mu\text{m}$  in pore diameter, the saturated amount of adsorbed ion depended on the pore size and increased linearly with the inverse of the pore diameter. This phenomenon can be explained by assuming the saturated amount of adsorbed ion in surface density,  $\Gamma_0$ , is constant. The charge density determined from the membrane potential is, however, in volume density. The saturated amount of adsorbed ion within the pore is given by  $4\Gamma_0/d_p$  in volume density where  $d_p$  is pore diameter. For the membrane of 8.0 and 1.2  $\mu\text{m}$  in pore diameter, the saturated amount of adsorbed ion in volume density became negligibly small and we could not detect the effective membrane charge due to the ion adsorption. For the membranes of 0.8 to 0.1  $\mu\text{m}$  in pore diameter, the membrane charge density at saturation was inversely proportional to the pore diameter  $d_p$ . It was, therefore, concluded that the surface charge density,  $\Gamma_0$ , was constant, not depending on the pore diameter in this region.

## 685.F1 FIELD-INDUCED TWO AND THREE DIMENSIONAL COLLOIDAL CRYSTALS

M. Trau<sup>1</sup>, D.A. Saville<sup>2</sup> and I.A. Aksay<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Queensland, Brisbane Qld. 4072, Australia.

<sup>2</sup>Department of Chemical Engineering, Princeton University, Princeton, NJ 08544, USA.

Electrical forces derived from polarization and free charge effects engender fluid motion in non-homogeneous liquids; most extant work involves macroscopic interfaces. Using video microscopy, we have studied configurations involving small particles dispersed in aqueous solutions. Upon applying a potential to an electrode, particles are attracted to an electrode, as expected. Moreover, since the particles are stabilized electrostatically, one anticipates that repulsive forces between the particles cause the deposit to be rather disorganized. However, we found that by tailoring the field the particles could be assembled into a polycrystalline layer<sup>1</sup>. Further experimentation showed how to assemble two- and three-dimensional crystals. Once assembled, these may be coagulated to form permanent structures. A theory has been developed which

shows that the attractive force causing the dynamic assembly of individual particles into the crystal is due to electrohydrodynamic forces.

I. Trau, Saville, Aksay, *Science* 272,706 (1996).

## 686.F1 ELECTRIC SURFACE PROPERTIES OF PURPLE MEMBRANES IN PRESENCE OF BUFFER MOLECULES

N. Tuparev<sup>1</sup>, S. Taneva<sup>1</sup>, I.B. Petkanchin<sup>2</sup>

<sup>1</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria;*

<sup>2</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The electric properties of purple membranes (PM) in presence of bis-tris propane (BTP) and glycylglycine (Gly-Gly) buffer molecules were studied by means of electric light scattering and electrophoresis in order to understand the buffer produced additional components to the light-induced electric signals of bacteriorhodopsin (I). The permanent and induced dipole moments were studied at different pH, buffer concentrations and ionic strengths. Upon addition of BTP the permanent and induced dipole moments of PM increase with pH increase, while in the presence of Gly-Gly the opposite effect is observed. The electric moments of PM have significantly lower values upon Gly-Gly than BTP addition. This effect is observed at buffer concentrations producing maximal changes in the electric signal waveform. PM suspensions treated with BTP or Gly-Gly give changes in electrophoretic mobility in different directions. The buffers-induced changes in the PM surface electric properties can be attributed to different distribution and alignment of the negatively charged Gly-Gly and positively charged BTP molecules in the vicinity of the membrane surfaces.

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I. S. Liu, M. Kono and T. Ebrey; *Biophys. J.*, 60, 204-216, (1991)

## 687.F1 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY ANALYSIS OF ENARGITE ELECTRODES

P. Velazquez<sup>1</sup>, H. Gómez<sup>1</sup>, D. Leinen<sup>2</sup>, J.R. Ramos-Barrado<sup>2</sup>

<sup>1</sup>*Instituto Químico, Universidad Católica de Valparaíso, Chile*

<sup>2</sup>*Departamentos de Física Aplicada, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain*

Electrochemical Impedance Spectroscopy (EIS) is a powerful technique for studying electrical and electrochemical properties of large variety of systems. Concerning to the use of EIS to study electrodes, the electric surface behavior, bulk and interfacial properties of the electrode/electrolyte system can be determined. The enargite ( $\text{Cu}_3\text{AsS}_4$ ) electrodes has been studied by this method, using an EI Solartron 1286 and a FRA Solartron 1255 controlled by computer, in a borate solution for different oxidation and reduction potentials.

The results can be interpreted from a modified Randles equivalent circuit. From these results, the variation of charge transfer electrical resistance of the redox reaction, the double layer capacitance and others characteristic parameters with potentials was considered.

## 688.F1 CYCLIC VOLTAMMETRIC ANALYSIS AND XPS OF ENARGITE ELECTRODES

P. Velazquez<sup>1</sup>, H. Gómez<sup>1</sup>, D. Leinen<sup>2</sup>, J.R. Ramos-Barrado<sup>2</sup>

<sup>1</sup>*Instituto Químico, Universidad Católica de Valparaíso, Chile*

<sup>2</sup>*Dept. de Física Aplicada, Facultad de Ciencias, Universidad de Málaga, E-29071 Málaga, Spain*

Cyclic voltammeter (CV) is an usual technique for measuring redox events and it can be used to study the electrochemical behavior of species diffusing to an electrode surface and the bulk properties of

material in or on electrodes and characterizing the electric surface properties. CV has been applied to study the redox process in an enargite ( $\text{Cu}_3\text{AsS}_4$ ) electrode in a borate buffer solution. From the experimental results we can determine the different copper oxides in the electrode surface, X ray photoelectrons spectroscopy (XPS) and F.T.I.R. before and after the electrochemical treatment at oxidation and reduction potential permits us to confirm these results.

## 689.F1 SURFACE ELECTRO-CONDUCTIVITY STUDY IN COLLOIDS BY ELECTRO-ORIENTATIONAL METHODS

V.V. Vojtylov, T.Yu. Zernova, A.A.Trusov

*Faculty of physics, St. Petersburg State University, 198904, Russia*

Specific surface electro-conductivity is an important characteristic of electric double layer and surface structure. The electro-orientational measuring of it can be successful in the case of the applying of alternating electric field to the system under study and the investigating of the induced anisotropy. Field frequencies must be high enough to exclude the influence of permanent dipole on the orientation of the colloidal particles. These methods have permitted to check the theory of particle polarisability that comprises its surface electro-conductivity. Important peculiarity of the above mentioned methods is the adaptability them for the polydisperse systems that are being studied.

Effectiveness of this scientific approach has been demonstrated when measuring of various disperse systems surface electro-conductivity value and investigating surfactant influence on particle surface. The joined conductometric anisotropy and electro-kinetic study did clear the interrelationship between electro-kinetic potential and surface electro-conductivity, namely these characteristics clarify the electric structure of colloid particle surfaces.

## 690.F1 A NEW CONTACT ANGLE MEASUREMENT TECHNIQUE BY ANALYSIS OF CAPILLARY RISE PROFILE AROUND A CYLINDER (ACRPAC)

Yongan Gu and Dongqing Li

*Department of Mechanical Engineering, University of Alberta Edmonton, Alberta, Canada T6G 2G8*

A new experimental technique to determine the contact angles of capillary rise profiles around a conic cylinder is presented in this paper. In the experiment, a carefully coated conic glass cylinder was inserted vertically and slowly into a measuring liquid. Then a precise digital image of the partial capillary rise profile of the liquid around the conic cylinder was acquired and digitized by applying computer image processing and analysis techniques. From the digitized profiles of the liquid-vapour interface and the conic cylinder, the local inclination angle,  $\beta$ , and the local radius,  $R_c$ , of the conic cylinder at the three-phase contact circle were calculated directly. Furthermore, an objective function was constructed, which expresses the discrepancy between the physically observed capillary rise profile and the theoretically predicted curve, i.e., the curve representing a solution of the Laplace equation of capillarity. The contact angle of the capillary rise profile on the conic cylinder was used as an adjustable parameter in optimizing the objective function and determined once the minimum objective function was achieved. The accuracy of the measured contact angles is approximately  $0.1^\circ$ . In addition to local gravity, densities of liquid and vapour phases and the liquid-vapour surface tension, the input requirement is the digital information of the partial capillary rise profile which is provided by implementing a specially designed computer image analysis and digitization program.

This method was tested to measure the contact angles of four n-alkane liquids around cylindrical glass fibres coated with the FC725 material. The measured contact angles are in excellent agreement with those determined by the Wilhelmy plate technique. The present technique was also applied to study the dependence of contact angles on the geometry of the conic cylinder, i.e., on  $\cos\beta/R_c$ . The contact angles of the four n-alkane liquids on conic glass cylinder coated with the FC725 material were measured at different positions along the cylinder. The results were interpreted in terms of the line tension effect. The calculated line tensions were positive and of the order of  $1 \mu\text{J/m}$ , consistent with the published data for the similar solid-liquid systems using the sessile drop method. Particularly, the contact angle without the line tension

effect for a given solid-liquid system can be measured directly by this method. The validity of this contact angle and line tension in the paper was also confirmed by the Axisymmetric Drop Shape Analysis (ADSA) technique. Finally, this new technique is especially suitable to study wetting and spreading phenomena of a liquid on fibres as most natural and artificial fibres are porous and their shapes may vary along the length direction. As an important application, this technique was applied to measure the advancing and receding contact angles of three liquids on six cylindrical polymeric fibre samples which were used as capillary membranes in haemodialysis. A general user-oriented computer program to implement the technique was developed.

## **691.F1 ELECTRO-ORIENTATIONAL STUDY ON EFFECT OF SOME BACTERIOPHAGES AND BACTERIOCINES ON MICROORGANISMS**

**Zhilenkov E.L., Fomchenkov V.M., Vybornova L.A., Blagodatskikh A.Ya., Gavryushkin A. V.**

*State Research Center for Applied Microbiology, Moscow region, Obolensk, Russia*

In the present study, using electro-orientational spectroscopy for rapid characterization of the interaction between phages or bacteriocines and sensitive, lysogenic and foreign bacteria was evaluated. Along with electro-orientational spectroscopy, electron microscopy and other conventional microbiological methods were applied for experiments. It was observed that the EO-spectrum of sensitive cells of *Pseudomonas aeruginosa* treated with phage Ø04 (morphotype B1) different from that of the control at all frequencies under research.

Phages Ø04 were adsorbed on Ø04-lysogenic cells of *Pseudomonas aeruginosa* but without injecting DNA. The change of the EO-effect in the system was recorded at average frequencies only. The interaction of pyocine R, bacteriocin R572, with a sensitive cell of *Pseudomonas aeruginosa* resulted in changes both of the superficial electrostatic potential and transmembrane one. Studing the high frequency region of the spectrum made it possible to identify pyocin-induced damages in cells. The results obtained correlated with those obtained by Japanese researchers and suggested a structural change of cell membranes of *Pseudomonas aeruginosa* (Uratani, Kageyama, 1977).

*Pseudomonas aeruginosa* phage Ø05 (morphotype C1) was adsorbed on a foreign cell of *Y. pestis* EV. The EO-spectrum of the system Ø05-*Y. pestis* was characterized by variations within a low frequency region.

In all studies, there was recorded good correlation between electro-orientational spectroscopic data and those obtained by electron microscopy or other methods. Based on the findings it is considered that the electro-orientational method is a useful tool for rapid characterization of the interaction of phages or bacteriocines with different microorganisms.

## **692.F1 EFFECTS OF CHANGES IN THE CONCENTRATION OF BACKGROUND ELECTROLYTE ON THE POINT OF ZERO CHARGE AND THE ISOELECTRIC POINT OF SOLID OXIDES IN AQUEOUS SOLUTIONS.**

**A.N. Zhukov**

*St. Petersburg State University, Chemical Faculty, Universitetsky pr. 2, Petrodvoretz,  
198904 St. Petersburg, Russia.*

The triple layer model of solid oxide/aqueous solution interface was used to study the effects of changes in the concentration (C) of simple background 1:1 electrolyte on the point of zero charge (PZC) and the isoelectric point (IEP) of solid oxides in aqueous solutions. Two surface reactions of deprotonisation and protonisation of amphoteric surface hydroxyl groups (intrinsic constants  $K_{a1}$  and  $K_{a2}$ ) and two reactions of the binding of background electrolyte ions  $M^+$  and  $A^-$  with ionized surface hydroxyl groups (intrinsic binding constant  $K_M$  and  $K_A$ ) were considered and corresponding equations of the mass action law were used to obtain two analytical expressions for the PZC and IEP values as the functions of  $K_{a1}$ ,  $K_{a2}$ ,  $K_M$ ,  $K_A$  and C. The analysis of these expressions shows that when  $K_M$  is more (less) than  $K_A$  and C increases, the PZC moves to the lower (higher) values and the IEP moves in opposite directions with respect to the pristine value equal to

$0.5(pK_{a1}+pK_{a2})$ . The model predictions are in qualitative agreement with the experimentally observed shifts of PZC and IEP occurring in the cases of the specific adsorption of ions.

## 693.F1 ELECTRICAL PROPERTIES OF SOME SOLID OXIDE/NON-AQUEOUS ELECTROLYTE SOLUTION INTERFACES

A.N. Zhukov, V.I. Varzhel

*St. Petersburg State University, Chemical Faculty,  
Universitetskyy pr. 2, Petrodvoretz, 198904 St. Petersburg, Russia.*

The origin of the surface charge and electrical surface properties of solid inorganic oxides in aqueous electrolyte solutions are fairly well known. Main mechanisms of the generation of the surface charge in such systems are either the loss ( $-\text{SO}^-$ ) or the gain ( $\text{SOH}_2^+$ ) of proton by surface hydroxilic groups ( $-\text{SOH}$ ) due to their reactions of acid-base equilibria with water and the adsorption of the background electrolyte ions ( $\text{K}^+$  and  $\text{A}^-$ ) on ionized hydroxilic groups ( $-\text{SO}^--\text{K}^+$  and  $-\text{SOH}_2^+-\text{A}^-$ ). But the mechanisms operating in non-aqueous solutions are not clearly understood. The main objective of this work was to study and to compare the electrical surface properties (electrokinetic potential  $\zeta$  and charge  $Q$ ; ion adsorption  $\Gamma$ ; surface conductivity  $K_s$ ) of three powdery oxides  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  in  $C=10^{-5}$ - $10^{-2}$  M LiBr, KBr and NaBr solutions in four solvents differing from water: two amphoteric solvents (ethanol, 1-butanol) and two aprotic solvents (dimethylsulfoxide (DMSO) and dimethylformamide (DMFA)).

The main features of the experimental results are the following: values of  $\zeta$  and  $Q$  in the diluted solutions are negative (excepting  $\text{Al}_2\text{O}_3$  in BuOH) and they become more positive in the order  $\text{SiO}_2 < \text{TiO}_2 < \text{Al}_2\text{O}_3$ ; the increase of electrolyte concentration brings to the more positive values of  $Q$  while depending on the nature of electrolyte  $\text{LiBr} < \text{NaBr} < \text{KBr}$ ; the increase of electrolyte concentration gives the inversion of the sign of  $Q$ ; the isotherms of cation and anion adsorption  $\Gamma(C)$  show their non-equivalent character (adsorption of cations is always greater than of anions and increases in the order  $\text{Li} < \text{Na} < \text{K}$ ); the specific surface conductivity of all these systems is several orders higher than the values calculated according to Bikerman theory and has non-zero values at the isoelectric points.

The analysis of the results brings to the following view on the mechanism of the charge formation on oxides in the electrolyte solutions in the studied solvents. The origin of the surface charge in such protic liquids as alcohols is due to the acid-base interactions similar to that in water and involving proton as a potential-determining ion. Value of this charge in the diluted solutions is defined by relative acidity of both the liquids ( $\text{EtOH} > \text{BuOH}$ ) and the surface OH-groups of the oxides ( $\text{SiO}_2 > \text{TiO}_2 > \text{Al}_2\text{O}_3$ ). The surface charge on the oxides in aprotic liquids is determined by the donor-acceptor interactions. In the case of DMSO and DMFA with their high donicity, this charge is formed by the proton dissociation of the OH-groups. The adsorption of background electrolyte ions also influences not only the value but the sign of the electrokinetic charge. The increase of the negative charge of  $Q$  with the growth of electrolyte concentration and then its sign inversion may be explained by the fact that these ions are adsorbed not only on the ionized OH-groups ( $-\text{SO}^-$ ,  $-\text{SOH}_2^+$ ) but also on non-ionized ones ( $-\text{SOH}$ ). That means their specific interactions with the surface groups are mainly determined by the solvation ratio of ions. The surface conductivity in the studied systems is due to the mobility of all ionic species in diffuse and Stern layers.

## 694.F2 PHOTOINDUCED COLLECTIVE INTERACTIONS OF COLLOID PARTICLES

V.V. Andreev and G.G. Telegin

*Chuvash State University, Cheboksary, Russia*

At the present time the processes of interaction of colloid particles in the field of laser radiation have attracted much interest. In case collective interaction of atoms among themselves leads to nonlinear interaction with external laser radiation at low intensity [1-3]. In this work the influence of optical field effect to collective behaviour of atoms on the solid surface and colloid particles was investigated. It was assumed that initial distribution of particles ensemble is uniform, but distribution of optical radiation intensity by cross section has Gauss forms. Laser radiation is directed to the solid surface or to the particles in volume. The equation, describing surface density of atoms or volume density of particles contains drifting

and diffusional components. They are the results of collective lateral interaction dipoles induced by laser radiation. It is shown, that this leads to nonuniform distribution of atoms and particles depending on sign of interaction potential of dipoles. They can observe on illuminational area "craters" or "mounds" on surface and high- or low- particle density structure in colloid.

The obtained results show the possibility of nonuniform disperse particle structures formation in colloids by use of coherent light field.

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## 695.F2 ELECTRO-OPTICAL BEHAVIOR OF AEROSIL PARTICLES IN PRESENCE OF POLYETHYLENIMINE

M. Buleva, I. B. Petkanchin

*Bulgarian Academy of Sciences, Institute of Physical Chemistry, Sofia 1113, Bulgaria*

Aqueous dispersions from Aerosil OX in presence of polyethylenimine (PEI) (product of BASF - Germany) with molecular weight 8000-10000 are studied by electric light scattering and microelectrophoresis. The charge of polyions is changed by pH at constant ionic strength. A significant differences are observed in electro-optical dependences and rotational diffusion coefficients ( $D_r$ ) at low and high PEI charge resp. at pH 6 and pH 9. It has to be noted that the adsorption proceeds on recharged surface of the particles (positive charged) in both cases.

At high polyions' charge (pH 6) the electro-optical effect, proportional to the surface electric polarizability ( $\gamma$ ) increases with polyions concentration, and  $\gamma$  correlate with electrophoretic mobility increase. The rotational diffusion coefficients do not change compared with the "bare" particles, indicating a flat adsorption layer. A shift of the polarizability relaxation frequency to higher frequencies is observed as well. At lower polyions charge the increase of  $C_{PEI}$  does not influence the electro-optical effect and its relaxation frequency. In this case an increase of particle' relaxation time is observed compared to the "bare" particle and to those at pH 6. This can be explained with an increase of the adsorbed polymer layer thickness. The results obtained are discussed in the light of bulk properties of polyions and compared to the adsorbed state.

The work is financially supported by EC contract No CIPACT 923013.

## 696.F2 ADSORPTION OF POLYACRYLIC ACID ON $\alpha$ - $Al_2O_3$ COLLOID PARTICLES AS STUDIED BY ELECTRO-OPTICS

Maria Buleva<sup>1</sup>, Viktor Peikov<sup>1</sup>, Emile Pfefferkorn<sup>2</sup> and Ivana Petkanchin<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*Institute "Charles Sadron" (ICS-CNRS), 6, rue Baussingault, 67083 Strasbourg, France*

The adsorption of Polyacrylic Acid (PAA) on partially soluble  $\alpha$ - $Al_2O_3$  particles (Péchiney) is studied in aqueous dispersions containing  $Al^{+3}$  ions at pH 5 and constant ionic strength. The concentration of  $Al^{+3}$  ions,  $3 \times 10^{-4}$  N, corresponds to the equilibrium solubility of  $\alpha$ - $Al_2O_3$  at this pH. The adsorption mechanism depends on the degree of complexation between PAA and  $Al^{+3}$  ions. The adsorption is studied by means of Electric Light Scattering and Electrophoresis methods.

The adsorption of negatively charged PAA molecules overcompensates the positive surface charge of  $\alpha$ - $Al_2O_3$  particles, the isoelectric point (iep) being at adsorption density of  $\Gamma_{PAA} = 2.5$  mg/m<sup>2</sup>. The value of the  $\zeta$  potential changes sharply from positive to negative in a narrow concentration range in the vicinity of the iep. Outside this concentration range the suspension is electrically stabilized and  $\zeta$  potential is almost



independent of the adsorption density. Above the iep, the absolute value of  $\zeta$  remains about two times smaller than the value measured below the iep.

The value of the electrooptical effect, proportional to the surface electric polarizability of the particles ( $\gamma$ ), follows the dependence of  $\zeta$  potential as a function of the adsorption density with a minimum at the iep. Above the iep, the adsorption strongly changes the shape of the frequency dependence of the electric polarizability. The plateau in the kHz frequency region becomes shorter and shifts toward the lower frequencies. The relaxation frequency of the high frequency dispersion of  $\gamma$  decreases as a manifestation of the decreased mobility of the ions taking part in the polarization of the electric double layer. We expect that the present study would shed lights on the effect of the adsorption on the surface electric properties and the structure of the electric double layer of the alumina particles. The influence of the conformation of the adsorbed polyions on the stability and surface properties of the particles will be discussed.

## 697.F2

### ELECTROPHYSICAL ANALYSIS OF CELLS BY ELECTROOPTICAL METHOD

Bunin V.D., Voloshin A.G.

*NRC for applied microbiology, 142289, Obolensk, Moscow reg., Russia*

Electrophysical analysis of cells used for the monitoring and optimization of technologies for the production of preparations on the base of the viable cells; control of intracellular biosynthesis product accumulation in genetically modified cells; calculation of substance concentration by means of evaluation of electrophysical parameters cell biotest system.

This type of analyses used interrelation between physiological function of cell and physical parameters of cell structures. Electrophysic alanalysis of cells based on its representation in the conjugate layers with different dielectrical ( $\epsilon_i = \epsilon_i + \sigma_i/j\omega$ ) and morphometrical ( $\Delta l_i$ ) parameters, where  $\epsilon_i$  - dielectric permeability and  $\sigma_i$  -electroconductivity of  $i$  layer respectively,  $\omega$  - frequency of electric field. Each layer corresponding to cell structure (cytoplasm, membrane, cell wall et).

Source data for the calculation of dielectrical and morphometrical parameters of cell structure is the Frequency Dispersion of Anisotropy Polarisability (FDAP) -  $\{d\alpha(\omega_i)\}$ . This function result in electrooptical measurement of  $d\alpha(\omega_i)$  on the series of electric field frequencies ( $\omega_i$ ) (1,...N) from 10 kHz to 30mHz. If cell orientation degree is weak and variations  $dD$  of optical density  $D$  are measured, that value of FDAP<sub>i</sub> function is equal:  $d\alpha(\omega_i) = dD/(D \cdot \tau \cdot G_c \cdot E^2)$  where  $\tau$  - optical transmission of cell sample,  $G_c$  weight mean light scattering section of the cells. Calculation of  $\epsilon_i$  and  $\Delta l_i$  of cell structures based on the usage of cell model as layer structures; theory of bulk polarisability, polarisability of cell substances on the cell structures boundaries after electric field action; calculation of FDPA function for the cell model and usage of algorithm minimizing the distinction between model and experimental functions FDPA.

The results of electrophysical analysis of cells in mentioned above areas are described.

## 698.F2

### OPTICAL DETECTION OF MEMBRANE DIPOLE POTENTIAL

Ronald J. Clarke and David J. Kane

*Department of Biophysical Chemistry, Max-Planck-Institut für Biophysik,  
D-60596 Frankfurt am Main, Germany*

Fluorescent sryrlypyridinium dyes have recently been suggested as probes of the membrane dipole potential and of the kinetics of electrogenic ion pumps. It is necessary, however, to be able to confidently attribute observed fluorescence changes to electrical effects alone and avoid interference from changes in membrane fluidity. Furthermore, the effect of the dyes themselves on the dipole potential must be investigated. The effect of membrane fluidity on the fluorescence excitation and emission spectra of the dyes RH421 and di-8-ANEPPS have been investigated in lipid vesicles by temperature scans between 15 and 60°C. Both dyes show significant temperature-dependent shifts of their excitation spectra, the magnitude of which depend on the emission wavelength and on the lipid structure. In order to eliminate membrane fluidity effects, fluorescence must be detected at the red edge of the emission spectrum; in this case 670 nm. In order

to avoid dye-induced shifts of the excitation spectra of membrane-bound dye, an excess molar ratio of lipid to dye of at least 200 fold is necessary. Fluorescence ratio measurements indicate qualitatively that dimyristoylphosphatidylcholine has a significantly higher dipole potential than that of dioleoylphosphatidylcholine.

## 699.F2

### THEORY AND EXPERIMENT OF LIGHT GRADIENT IN SPHERICAL PHOTOSYNTHETIC SYSTEMS

A. Dobek<sup>1</sup>, G. Paillotin<sup>2</sup>, J. Gapinski<sup>1</sup>, W. Leibl<sup>3</sup>, K. Gibasiewicz<sup>1</sup>, J. Breton<sup>3</sup>

<sup>1</sup>*Institute of Physics, A. Mickiewicz University, Poznan, Poland,*

<sup>2</sup>*INRA Paris, France,*

<sup>3</sup>*Section de Bioenergetique, DBCM, CEA Saclay, France*

The paper reports results of theoretical and experimental studies of the optical and dielectric properties of spherical photosynthetic membranes. For the first time the approach based on the use of polar co-ordinates has been adapted for theoretical description of biological systems of spherical symmetry. The obtained formulae were used for calculation of light intensity distribution in such systems and the results were verified in a comparison with results of the light-gradient experiment. The formulae derived within the same approach were fit to the corresponding experimental data obtained for EDTA - vesicles and swollen thylakoids. In the case of EDTA - vesicles, the negative polarity (due to normal light gradient) was observed in the blue range of the absorption spectrum, while the positive one, corresponding to the inverse light gradient, at  $\lambda = 530$  and  $\lambda = 682$  nm. The signs of the photovoltage polarity measured in large blebs (swollen thylakoids) are the same as those obtained for samples of the whole chloroplasts with the only difference in the amplitudes. The fits of the theoretical formulae to the photovoltage amplitudes measured as a function of light wavelength, enabled drawing the values of certain parameters concerning the photosynthetic membrane and spherical vesicle. These parameters include geometrical and stoichiometrical data: membrane thickness  $L=5.1$  nm, EDTA vesicle radius  $R_1=100$  nm, swollen thylakoid (bleb) radius  $R_1=1000$  nm, chlorophyll concentration in the membrane  $[Chl] = 0.45$  M, and electric and optical characteristics: effective dipole moment photo-generated in (PSI and PSII) RC  $m^{eff}=5.9 \times 10^{-28}$  Cm, dielectric constant of RC,  $\epsilon_s=3$  indicated for ps time range in the direction of electron transfer (perpendicular to surface of the membrane), refractive index of the photosynthetic membrane estimated far from the absorption band for the light propagating perpendicular and parallel to the membrane surface,  $n_r=1.42$  and  $n_n=1.59$ , respectively. These values determine the birefringence of the biological membrane  $\Delta n=n_n - n_r=0.17$ . Values of the imaginary parts of normal and tangential component of dielectric constant found in the red range ( $650\text{nm} < \lambda < 730\text{nm}$ ) of photosynthetic membrane absorption spectrum support the previous findings that the pigments absorbing in this region have their transition moments oriented nearly in the plane of the membrane. For other wavelengths, the transition moments for absorption are much less dichroic, which is consistent with our photovoltage measurements at  $\lambda = 435.6$  nm and  $\lambda = 530$  nm.

## 700.F2

### THE MECHANISM OF LUMINESCENCE BY LASER LIGHT ON AQUEOUS SOLUTION SURFACTANTS

P.K. Khabibullaev, Sh.I. Mamatkulov, YU.V. Pakharukov, A.A. Saidov

*Heat Physics Department of the AS of Uzbekistan, 700135 Katartal str. 28, Tashkent*

In the work the influence of laser light on donor centers of molecule SAS is investigated. Knocked out electron being in water locates on the acceptor level- a trap created by molecules of water. The return transition of electron from trap in the hole left on ionized SAS molecule will give way to recombination of electron with its hole as a result of which photon is highlighted. The spectral density of luminescence's intensity in this case can be described by expression:

$$I(\epsilon) = I_0 \sigma_i \left( 4\pi c l^3 / 3\epsilon_0 V \right) e^{[-0.4(\epsilon_r - \epsilon)/\epsilon]} \\ \epsilon_c = \epsilon_0 \ln(4 / 3\pi R_c^3 N_a)$$

Where  $N_a$  - concentration of the acceptors levels,  $\sigma_i$  - the section of ionization,  $l$  - the size of SAS molecule,  $I_0$  - the intensity of laser light,  $V$  - volume,  $c$  - the concentration of SAS molecules. In case of micelle formation

the section of ionization for micelle  $\sigma_i^m$  is less than  $\sigma_i$  because of larger communication of electron with donor's center, but size micelle is  $R=2l$ . As a result in the point of micellezation the jump of luminescence intensity proportionally to  $R^3/l^3 \approx 8$  is observed, that is very well agreed with the results of experiment where the effect of laser light on water solution's n-oktil -benzene sulphonate is investigated.

## 701.F2 ELECTRO-OPTICS OF COLLOIDAL CRYSTALS STUDIED BY THE REFLECTION SPECTROSCOPY

Tsuneeo Okubo, Akira Tsuchida, Shinnichi Okada, Tomofumi Tanahashi and Atsue Iwata

*Department of Applied Chemistry, Gifu University, Gifu 501-11, Japan*

Colloidal crystals are the suspensions in which colloidal particles distribute regularly like typical crystals such as metals and protein crystals. We observed very large size of ("giant") colloidal single crystals in the highly diluted and exhaustively deionized suspensions of monodisperse polystyrene and silica spheres. Crystal structure, morphology, phase transition, crystal growth kinetics and others have been studied in our laboratory. Colloidal crystals emit the brilliant iridescent light by the Bragg diffraction, since the inter-sphere distance are just in the range of light wave length. Purpose of this work is to study the electro-optic responses of colloidal crystals by the reflection spectroscopy in an a.c. electric fields.

Colloidal silica spheres, CS-81 (diameter= 103 nm  $\pm$  13.2nm) and CS-91 (diameter=110nm $\pm$ 4.5nm) which were deionized thoroughly with the ion-exchange resins more than three years, were used. These samples were gifts from Catalyst & Chemicals Ind.Co.(Tokyo). Electro-optic signals were recorded on a digital oscilloscope (model DL-1300, 4 channel, 100MHz, Yokogawa Electronics) through photo-multiplier tube connected with a Y-type optical fibre. Krohn-Hite oscillator (model 4025) was used. Time-resolved reflection spectra were recorded on a multi-channel spectrophotometer, PMA-50, C5094 (Hamamatsu Photonics). Reflection signals were taken using three types optical cells, (i) a cell consisting of two parallel plates (optical pathlength= 3mm) coated with electrically conducting membranes, (ii) a cylindrical Pyrex cell containing inner two sets of parallel platinum plates (four plates, electrode pathlength= 8mm), and (iii) a H-type Pyrex cell with two parallel platinum plates (pathlength= 55mm). Light source was a halogen lamp (model PHL-50, Mejiro Precision Co).

(1) Waveforms observed in a low-frequency range from 0.02 to 10 Hz showed a significant phase difference from the original applied field. This difference was more significant for higher field strengths and/or lower frequencies.

(2) Amplitudes of the waveforms responded were larger for the higher applied voltage and low frequencies in most cases. The amplitude depended on the location of the observation, where the reflection signals were taken. Even out-side area from the electrodes strong signals were obtained, and the amplitudes changed oscillatory in the whole surface area of the cell. This supports strongly that the electro-optic effects observed in this work were originated from the shear waves of colloidal crystals induced by the electric field just like *phonon*.

(3) In a high frequencies, in low applied field strengths and in aqueous suspensions, higher order harmonics has been rarely observed. However, substantial second-order harmonics was obtained at low frequencies and high electric fields especially in the deionized ethanol and ethyleneglycol with the ion-exchange resins. In some cases, the third-order and even fourth order harmonics effects were also observed. These harmonics effects were further analyzed with the Fourier transform of the reflection signals and also with the X-Y type plots between the waves applied and responded.

(4) The oscillating peak shifts of the reflection spectra to longer and shorter wavelengths were observed depending on the polarity of the oscillating electric fields. This oscillation in the reflection peaks is clarified to be the main cause of the harmonics effects.

(5) The electro-optic effects observed in this work have direct relationship with information obtained from the conventional electro-optics measurements using electric light-scattering technique and the dynamic light-scattering measurements.

## 702.F2 DIRECT, CONVERSE AND PHOTO FLEXOELECTRIC EFFECT IN BILAYER LIPID MEMBRANES

A.G. Petrov

*Biomolecular Layers Department, Institute of Solid State Physics,  
Bulgarian Academy of Sciences, Sofia 1784, Bulgaria*

Flexoelectricity provides a reciprocal relationship between electrical and mechanical degree of freedom of a surfactant bilayer, i.e. between bilayer polarization (or transbilayer voltage) and bilayer curvature (or bending stress). Both direct flexoeffect (curvature-induced polarization) and converse flexoeffect (voltage-induced bending stresses) are expected based on the general theory of flexoelectricity [1]. Using a thermodynamic description of these effects, we show that the manifestation of converse flexoelectricity in two-dimensional systems like bilayer lipid membranes (BLM) is strongly impeded by a mechanical constraint, the membrane tension. The registration of the effect under non vanishing tension then requires a highly sensitive experimental technique.

Furthermore, we report on an important breakthrough in flexoelectric, experiments: the laser stroboscopic interferometry (Todorov, Petrov & Fendler). This technique, using a mode-locked, pulse-picked, and Q-switched second harmonic of a Nd:YAG laser, was applied for the real-time determination of BLM curvature during its oscillation in the frequency range of 100Hz to 1KHz. The curvature oscillations were mechanically excited in the case of the direct flexoeffect and electrically excited in the case of the converse flexoeffect.

The application of real-time stroboscopic interferometry resulted in the first measurement of the flexoelectric coefficient of a purely dipolar synthetic lipid, glycerol monooleate ( $4.3 \times 10^{-20}$  C); the refined data on the flexoelectric coefficient of a zwitterionic phospholipid, egg lecithin, bearing a weak negative surface charge ( $1.3 \times 10^{-18}$  C); and the first measurements of the flexoelectric coefficient of a strongly negatively charged phospholipid, phosphatidyl serine ( $2 \times 10^{-18}$  C, largely pH independent). Converse flexoeffect was demonstrated for the first time in a BLM of phosphatidyl serine (PS), surface stabilized by the adsorption of uranyl acetate ( $UA^{2+}$ ) ions that result in a high surface dipole moment.

By confronting the experimental data to the theory, we draw the conclusion that the underlying molecular mechanism of flexoelectricity is a shift of the surface charge equilibrium under bending, expressed by the area derivative of partial electric charge per lipid head. The average value of the converse flexoelectric coefficient of a PS-UA membrane,  $(15.1 \pm 2.9) \times 10^{-18}$  C, agrees reasonably well with that reported previously for the direct flexoelectric coefficient of an UA-modified BLM  $(12.0 \pm 1.2) \times 10^{-18}$  C, demonstrating the validity of the Maxwell relation. Thus, both manifestations of flexoelectricity in BLMs have now received an experimental confirmation.

A new effect involving also another, optical degree of freedom of BLM, i.e. photo-flexoelectricity, is discovered by us very recently (Spassova, Petrov & Fendler). It is observed in a composite BLM containing *in situ* generated photo-semiconductor CdS nanosized particles (mimicking integral proteins of bio-membranes) upon bandgap illumination. Light-dependent flexoelectric response is rationalized in terms of curvature-modulated BLM photo potential.

Possible consequences of these new effects for the physicochemistry of colloid systems with flexible interfaces and for membrane biophysics will be discussed [1].

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## 703.F2 ELECTRO-OPTICS OF COLLOID PARTICLES IN POLYELECTROLYTE SOLUTIONS

Ts. Radeva

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Light scattering in the presence of an electric field is utilized for studying the electric properties and structure of colloid-polyelectrolyte surface layers.

The superequivalent adsorption of polyelectrolytes on oppositely charged colloid particles is found to cause a peculiar electro-optical behavior of their stabilized suspensions. An additional low-frequency

effect appears due to polyelectrolyte adsorption (different from the effect of particles rotation), which is attributed to polarization of loosely bound counterions of reduced mobility in comparison to the mobility of free ions. Examples are given that counterion condensation occurs not only on the highly charged polyions but also on sites formed by folding of the adsorbed weakly charged polymer chains. As in the suspensions without polymer, the high-frequency electro-optical effect is attributed to the free counterions polarization in an electric field.

The frequency behavior of the electro-optical effect from suspensions containing polyelectrolytes with counterions mixtures is explained in accordance with the theory that the fraction of free counterions increases with increasing the equivalent fraction of strongly bound counterions. Immobility of strongly (tightly) bound counterions at low field strengths is supposed in these considerations.

Experimentally obtained small values of the adsorbed layer thicknesses (determined from the decrease of the particle diffusion coefficients in presence of polymer) are discussed in terms of existing theories, predicting conformational transitions in the adsorbed polyions due to strong electrostatic interaction with the adsorbent surface.

The variations in suspension stability because of the polyelectrolyte adsorption are found to correlate with the particle electric surface properties.

## **704.F2      ELECTRIC PROPERTIES AND CONFORMATION OF POLYETHYLENIMINE AT HEMATITE/AQUEOUS SOLUTION INTERFACE**

**Ts. Radeva and I. Petkanchin**

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The variations of electro-optical behavior and pH of ellipsoidal hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) particles are investigated in presence of polyethylenimine (PEI). Suspension stability and particle electrophoretic mobility are also followed. Considerable shift of pH and the particle isoelectric point is found at extremely low PEI concentrations, indicating that nearly all amino groups of unfolded PEI molecules contact with the oxide surface. The small value of the polymer layer thickness in stabilized suspension (from electro-optical data) shows "flattening" of the PEI molecules even at higher polymer adsorption.

Similar electro-optical behavior of suspensions with either a positive or a negative oxide particles in an excess of PEI indicates that the particles assume the charge characteristic of the polymer. Reduced counterion mobility, found in both systems, is related to counterions condensation on the polyion surface and, possibly, to conformational transition in the adsorbed low-charged polymer molecules.

This work is supported by Contract CIPA CT 923013.

## **705.F2      COLLOID ELECTRO-OPTICS AS AN ADVANCED MODERN METHOD OF THE INVESTIGATION OF PARTICLE'S ELECTRO-SURFACE STRUCTURE**

**E. Rudakova, A. Spartakov, A. Trusov**

*Faculty of Physics, St. Petersburg State University, 198904, Russia*

Electro-optic phenomena in dispersed systems are connected with the orientation of the particles under the action of the external electric field. The last one is determined by the values of the permanent and induced dipole moments. Advanced and complex theoretical and experimental investigation of the particle's electric properties is put forward. The method of the particle's electric anisotropy determination is developed for the first time. This method is based on electro-optic phenomenon in three types of special rotating electric fields and it allows to study permanent and induced dipole moments separately. The principal new methods of stationary and transient electro-optic's phenomenon on investigations in weak and high fields are developed also. Electro-optic and conductometric methods of separate determination of particle's permanent electric dipole moment and electric polarizability are developed and adapted for studying the physico-chemical processes on the surface of the colloidal particles in real polydisperse systems, more exactly: the influence of ions and surfactants on the physico-chemical parameters of particle's surface and double electric layer. The problem of particle's size distribution function determination has been solved also. Thus the whole totality of suggested electro-optic methods essentially permits to study colloids in the wide range - from weak-

concentrated systems to dense pastes and from weak-conducting systems to the electrolytes. The information about electric and geometrical characteristics of colloidal particles permits to solve the problems of stability, aggregation and sedimentation of colloidal systems.

**706.F2****DEPENDENCE OF THE ELECTRICAL FIELD ON THE  
ELECTRO-OPTICAL EFFECT OF POLARIZATION OF  $\text{PbO}_2$** 

N. Saidi<sup>1</sup>, H. Saidi<sup>1</sup>, S.P. Stoylov<sup>2</sup>

<sup>1</sup>*Chemistry Processing Institute, University of Bejaia, 06000 Bejaia Algeria*

<sup>2</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

The electrical field strength has influenced the electro-optical effect of polarization of  $\text{PbO}_2$  in the solution of  $\text{H}_2\text{SO}_4$ :

- a) Under different concentrations of  $\text{H}_2\text{SO}_4$  solution;
- b) With the presence of Arsenic (1 g/l) in the solution of  $\text{H}_2\text{SO}_4$ .

We remark the increase of the concentration of the solution  $\text{H}_2\text{SO}_4$  (with and without the presence of Arsenic) and the electrical field, which result in the increase of the electro-optical of polarization. In both cases, we can calculate the electro-optical of polarization of the different solutions, and study the movement of the particles of  $\text{PbO}_2$  in the solution.

**707.F2****THE ROLE OF THE DOUBLE LAYER NONLINEAR POLARIZATION  
IN ELECTROORIENTATION**

O. Shramko, V. Shilov, T. Simonova

*Institute of Boicollodial Chemistry, National Academy of Science of Ukraine,  
85 Frunze St., 254080, Kyiv, Ukraine*

The electroorientation of the second order on an external field is related not only with the interaction between field and induced dipole moment of a particle. We have shown, that the interaction of the particle permanent quadrupole moment with a polarization electrical field which in the second order on external field has the quadrupole symmetry as to external field is so effective for electroorientation as a traditional mechanism. The traditional component of electroorientation is in the state of isopolarization. The alternative component is absent in the isoelectricalstate of the system. The correlation between traditional (torque  $M_1$ ) and new (torque  $M_2$ ) parts of the electroorientation is investigated for the spheroid with the double electric layer of great thickness. For experiment is essential the difference between both torques, traditional  $M_1$  and new  $M_2$ . Torque  $M_2$  caused by the particle permanent quadrupole moment is quadratic in the Stern potential,  $\psi_\delta$ , and inversely proportional to the Debye length,  $r_d$ . The  $M_1$  traditional torque dependence on the double layer parameters becomes less sensitive with the medium electroconductivity decrease. In the limiting case,  $r_d \ll a$ , ( $a$  is linear dimension of the particle) the  $M_1$  torque depends on the relationship of the polarities of both media only. The dependence of the torque (and consequently the dependence of the electroorientation) on the double layer parameters  $\psi_\delta$ , and  $r_d$  in case  $a \ll r_d$  indicates the dominated contribution of the interaction between nonlinear polarization and the particle permanent quadrupole moment.

**708.F2****LIGHTSCATTERING BY ELECTRO-ACOUSTIC WAVES  
IN COLLOIDAL SYSTEMS**

Maria Stoimenova<sup>1</sup> and Tsuneo Okubo<sup>2</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*Department of Applied Chemistry, Gifu University, Gifu 501-11, Japan*

The electric light scattering method is used for the detection of acoustic waves induced in colloidal crystals and liquids by low frequency electric pulses (1÷5). The method is sensitive to both density and shear modes and can be applied for the study of the liquid-crystalline phase transitions.

The electro-optic decay process is similar to the decay of the dynamic structure factor in photon correlation spectroscopy: interacting systems display biexponential decay; propagating low frequency shear modes induce oscillatory decay, related to self-resonance frequencies of the colloidal system.

The investigations on the electro-optic behaviour of isotropic (1+4) and anisotropic (5) colloidal systems demonstrate the possibility for separation of translation and rotation modes through electro-optic spectroscopy and the direct relation of electro-optic relaxation frequency to inter-particle interactions.

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## 709.F2 ELECTRO-ACOUSTIC WAVES IN ANISOTROPIC COLLOIDAL SYSTEMS

**Maria Stoimenova, Vassil Dimitrov and Aleksi Alekov**

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

Investigations on the electric light scattering effects displayed by colloidal suspensions of spherical particles (1,2) demonstrated the advantages of the electro-optic methods for analysis of the dynamic modes in colloidal systems. The contribution of electrically induced concentration and anisotropy fluctuations to the electro-optic response were demonstrated for colloidal systems of anisotropic particles (3). Particle orientation, conventionally related to surface polarisation processes, is influenced by density fluctuations as well (acoustic orientation). The correlation of electrically induced anisotropy and density fluctuations results in a complicated frequency dependence of the electro-optic responses. The field-induced dynamic structure factor can be analysed by the decay of the electro-optic response using the concepts applied in the analysis of photon correlation spectroscopy experiments.

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2. Stoimenova M., Okubo T., "Electro-Optic Spectroscopy of Colloidal Systems", in preparation.
3. Stoimenova M., Dimitrov V., Alekov A., "Electro-optics of Semidilute Dispersions: Influence of Electro-Acoustic Effects on the Electro-Optic Response of Colloidal Systems ", in preparation.

## 710.F2 DYNAMICS OF SURFACE CHARGE ON THE SOLID/LIQUID INTERFACE

**S.P. Stoylov, I. Petkanchin**

*Bulgarian Academy of Sciences, Institute of Physical Chemistry, Sofia 1113, Bulgaria*

The process of interfacial charge polarization is the physical background of many phenomena in colloids like electrophoresis, conductivity, dielectrics, electrooptics and dipole-phoresis. On the basis of these phenomena numerous experimental methods have been suggested which give information on the non-equilibrium electric surface properties of colloid particles. The consideration of the charge component through the induced dipole moment (electric polarizability), the charge inhomogeneity through the permanent dipole moment of the colloid particles represent next step of generalization of the electric properties of colloids following the average particle electric charge, which is the first largely studied

approximation. The non-charged component (Maxwell-Wagner polarization) seems to contribute much less to the total particle electric polarizability.

It is of considerable interest to understand the participation of the different parts of electric double layer (EDL) in the polarization mechanism as well as the influence of ionic conditions, adsorption of surface active substances, neutral polymers and polyelectrolytes. Clarifying the nature of charged and noncharged components in EDL is also needed as well as of the agreement of the theory with the experimental findings. A characteristic feature of the polarization mechanism is its dynamics, connected with charge mobility, the latter being important for interparticle interactions. The increase of the particle concentration leads to changes of the interfacial charge dynamics and distribution which reflect the real colloids systems in nature and technology. So it is possible to display the transition from very diluted systems ("ideal gas" approximation) where single particles properties are essential to concentrated disordered ("liquid" approximation) and ordered (colloid crystals) systems and to show the connection of the real electric properties of the single particles with the effective electric properties of the interacting colloid particles.

## 711.F2

### ELECTRIC LIGHT SCATTERING EFFECT OF ssDNA IN POLYMER SOLUTION

**Todorov, R., Starchev, K., Stoylov, S.**

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*

Capillary electrophoresis (CE) has rapidly become a powerful and attractive separation technique because of its sensitivity, rapidity and possibility of automation. CE is now routinely applied for the separation of DNA using polymer solutions as the separating matrix to avoid limitations from the gels, e.g. "trapping effect" and molecular aggregation. The application of a pulse field regime to CE enhance the size-dependent separation of DNA from few up to several megabases due to overcome the molecular orientation during standard electrophoresis. So far only few dates are published in this field and the mechanism is not yet fully understood. A more complete understanding of the pulse field electrophoresis in polymers and using new polymer solutions would permit the optimisation of experimental conditions for resolving DNA fragments that differ only slightly in size.

The electric light scattering is useful method for investigation of molecular orientation and aggregation in the presence of electric field. In the present study the electro-optical effects (EOE) of ssDNA in polymer solutions subjected on sinusoidal electric field are investigated by light scattering (observation angle  $90^\circ$ , white incident light). Polyacrylamide (PAA) in different concentrations is used as polymer matrix. The measurements are done in the electric field strength range up to 300V/cm and frequencies between 100 and 5000Hz.

The EOE of 55 $\mu$ g/ml single-stranded (ss) DNA in 1% PAA is growing in the field strength range 0-150V/cm for all studied frequencies. For all electric field strengths the light scattering effect is decreasing rapidly with the increasing of the frequency. The sinusoidal electric field with magnitude of 150V/cm is producing no significant effects on 1% PAA while in the presence of ssDNA the maximum effect is measured at pulses with 100Hz frequency. The dependence of EOE of ssDNA on polymer concentration is investigated at electric field strength 150V/cm with frequencies 500 and 1000Hz. The maximum effect was detected for 1% PAA for both frequencies and at 500 Hz it was higher than at 1 kHz. By measuring the decay of the EOE after switching off the applied field another quantity called the relaxation time of disorientation  $\tau$  is determined. It is decreasing with increasing of the polymer concentration.

This study has been supported by Grand BIOMED ERB CIP DCT 940402 of the EU.

## 712.F2

### REVERSING-PULSE ELECTRIC BIREFRINGENCE AND ELECTRIC DICHROISM OF COLLOIDAL SYSTEMS IN AQUEOUS MEDIA

**Kiwamu Yamaoka**

*Hiroshima Univ. (Prof. Em.) 2-2-805, 5-Chome Takamigaoka, Takaya, Higashi-Hiroshima 739-21, Japan*

The electric field orientation of colloidal suspensions and the interaction with the surrounding counterion can be best studied by the transient electrooptic methods. Recently we formulated a new



reversing-pulse electric birefringence (RPEB) theory for polyions with the axial symmetry, in which the relaxation time  $\tau$  of the polarization of ion-atmosphere along this axis was coupled with the overall molecular rotation around the transverse axis (1,2). The rod- and disklike molecules were assumed to possess three electric dipole moments, namely, the permanent  $\mu$ , ion-induced  $m$ , and electronic  $\Delta\alpha E$ . This root mean-square moment  $\langle m^2 \rangle^{1/2}$  is due to ion-fluctuation along the symmetry axis. The theoretical RPEB curve shows either a hump (maximum) or a dip (minimum) in the reverse and buildup (not always) processes according to the relative magnitude of three moments.

Experimentally, three typical colloidal suspensions of different particle shapes were measured in this work, i.e., the spherical polystyrene latex (3), the disklike montmorillonite clay (4,6,7), and the ellipsoidal  $\beta$ -FeOOH (5) systems. These samples showed the RPEB signal patterns, which were analyzed and compared with the theoretical curves. The importance of the ionic dipole moment and the effect of counterions will be discussed. The result on other colloidal systems will be briefly mentioned. The  $\beta$ -FeOOH particle and some dyes adsorbed on montmorillonite are dichroic and showed reversing-pulse electric dichroism in the spectral regions.

Part of this work was carried out in collaboration with Drs. R. Sasai and V. Peikov at Faculty of Science, Hiroshima University, and supported by grants-in-aid from the Ministry of Education, Science and Culture, Japan, and by a fellowship award (VP) from the Japan Society for Promotion of Science.

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## 713.F2 ELECTRO-OPTICAL BEHAVIOR OF COLLOID PARTICLES IN AGAROSE GELS

A.M. Zhivkov and S.P. Stoylov

*Institute of Physical Chemistry, Bulgarian Academy of Science, 1113 Sofia, Bulgaria*

The application of the electro-optic methods is limited by the electric conductivity of the medium, which leads to the appearance of convections in the colloid dispersion when an electric field is switched on. One of the possible approaches to the elimination of this problem is the exchange of the medium by a gel. The aim of this communication is to study the possibility of utilizing an agarose gel as a medium in the electro-optic investigation of colloid particles. The method of the electric birefringence is used for the study of the electro-optic behavior of agarose gels containing colloid particles of different sizes and forms. It is shown that the particles can be immobilized to different degree depending on the agarose concentration. This gives the possibility selectively to study only particles whose dimensions are below the dimensions of the pores. Thus it is possible to display the masked permanent dipole moment of the particles by their polydispersity. The effect of the gel on the rotational diffusion constant of the particles and on the frequency dependence of their electric polarizability is followed. At the sol-gel transition an optical anisotropy of the gel spontaneously arises, which grows with the agarose concentration and with the time. Theoretical expressions are suggested for the separation of the effects of spontaneous and electrically induced anisotropies. The spontaneous optical anisotropy leads to negative electro-optic effects even when there is no  $\lambda/4$ -plate at low frequencies of the electric field. The measurements of monodisperse colloid particles gives the possibility to determine the average pore dimensions and their size distributions. The found electro-optic effect of immobilized colloid particles at high field intensities is expected to give the possibility to investigate the local elasticity properties of the gel.

This study was realized with the financial help of the Contract European Commission - ERR GENE CT 930024/ERB CIPDCT 940402.

### 714.F3 CELL MODEL IN THE THEORY OF LOW-FREQUENCY DIELECTRIC DISPERSION IN CONCENTRATED DISPERSE SYSTEMS AND NON-HOMOGENEOUS ION-EXCHANGE RESINS

Yu. B. Borkovskaya, V. N. Shilov

*Institute of biocolloid Chemistry, Kiev, Ukraine*

The problem of the description of low-frequency dielectric properties of non-homogeneous ionic conductors (for example, water suspensions and plugs) reduces to the solution of the familiar set of equations for interconnected electric, diffusion and hydrodynamic fields with boundary conditions on the interfaces of the irregularities.

For dilute suspensions this problem simplifies to the solution of this set of equations in the vicinity of a single particle. This problem has been successfully solved previously by Shilov, Dukhin, O'Brien, De Lacey and White; low-frequency dielectric properties have been described quantitatively. For concentrated suspensions the exact solution of the problem is impossible and the simplified model must be used. The cell model is one of such models in which the mentioned above set of equations should be solved in the spherical cell with a particle in the centre. The cell model combines relative ease and the possibility to take into account such important properties of disperse systems as a pore curvity and a mutual influence of particles. The cell model appeared to be good for the description of high-frequency dielectric properties (Maxwell-Vagner polarisation) and for the description of hydrodynamic properties (Happel, Brenner).

In the report we have presented the results of the cell calculations of the characteristics of low-frequency dielectric dispersion for two systems - non-homogeneous ion-exchange resins and concentrated suspensions of charged nonconducting particles in electrolyte solutions. The strong dependence of a specific increment (the ratio of an increment to volume fraction) and a critical frequency on the concentration of dispersed phase has been found.

### 715.F3 LOW-FREQUENCY DISPERSION OF DIELECTRIC PERMEABILITY IN CHLORELLA VULGARIS AND BACILLUS CEREUS SUSPENSIONS

Borodinova T. I., Estrela-Llopis V. R. and Razilov I. A.

*Institute of Bio-Colloid Chemistry, National Academy of Sciences of Ukraine, Kiev, Ukraine*

The results are presented of complex investigations of dielectric permeability dispersion (DPD), dielectric losses and electrical conductivity (EC) as a function of volume share and concentration of potassium chloride electrolyte in suspensions of live and thermally inactivated *Chlorella vulgaris* and live *Bacillus cereus* cells, and their electrokinetic properties have been studied also.

Experimental installation has been set up on the basis of alternating current bridge. Electrokinetic measurements have been conducted using plane-parallel quartz cell of the closed type. Thermostated cylindrical cell with variable distance plane-parallel platinum electrodes has been used for measurements of dielectric parameters and EC.

Principal complication in conducting measurements in biological suspensions has been determined, which turned out to be the "shifting" behaviour of the cells, i.e. medium EC is increasing continuously due to secretion of extracellular metabolites (EM). Methods for overcoming this problem have been proposed. The measurements conducted have shown that DPD increment is less, while losses are greater for live cells than for inactivated ones. Stern layer potential  $\psi_\delta$  has been estimated independently from the low-frequency DPD limit and data on frequency and volume share electrical conductivity dependences within the limits of Shilov-Dukhin theory. It was shown that  $\xi$  potential decreases with electrolyte concentration, while  $\psi_\delta$  - potential increases, and moreover, for live cells  $\xi$  is more than that for dead ones, while  $\psi_\delta$  for live cells is less than  $\psi_\delta$  for dead ones. Thickness of the boundary layer has been calculated from the comparison of  $\xi$  and  $\psi_\delta$  values. The results obtained lead us to the conclusion on localization of mobile ions both in diffuse and densely-packed parts of double layer, and in the case of cell - within the boundaries of cell membrane.

This result accounts for the good correlation between estimates made on basis of  $\xi$  - potential (but not on basis of  $\psi_\delta$  - potential) with the use of DLVO theory and experimental data on cells heterocoagulation with gold sol and natural silica particles.

## 716.F3 MEASUREMENT OF PARTICLE TRANSLATIONS IN AC-FIELDS USING PHASE ANALYSIS LIGHT SCATTERING (PALS)

Peter Eppmann, Bernhard Prüger, Jan Gimsa

*Institute of Biology, Humboldt-University of Berlin, Berlin, Germany*

Particle polarization in ac-fields depends on field frequency, as well as on the dielectric properties of the suspension medium and the internal particle structures. Translational particle motion can be induced in inhomogeneous fields (dielectrophoresis, DP) or by traveling wave fields generated in arrays of repetitively arranged electrodes (traveling wave dielectrophoresis, TWDP). Common dielectric particle spectroscopy methods microscopically analyzes the frequency behavior of the induced motion to obtain information on the particles internal structures.

Phase analysis light scattering (PALS) was developed as an extension of the classical Laser-Doppler-Anemometry (LDA) for registration of extremely slow translational particle motion.

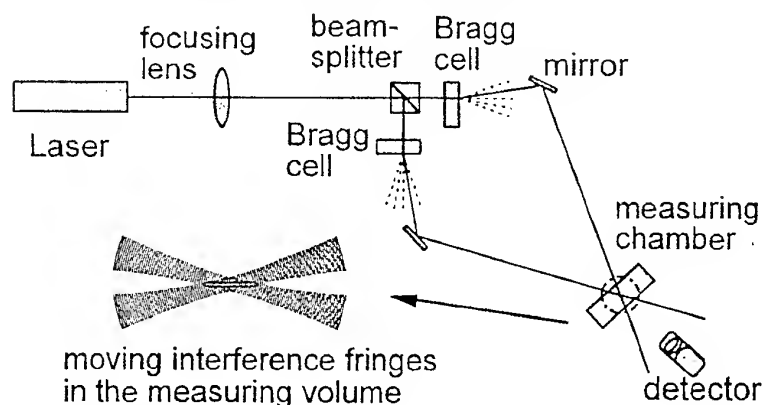


Fig. The optical light scattering setup used for particle measurements.

The figure schematically shows the optical setup of PALS-device. The measuring volume is defined by the interference pattern in the crossing region of the two Laser beams. The Bragg cells in the beam path introduce a small difference of the optical frequency of two beams in the kilohertz range. This small frequency shift causes a frequency offset in the scattered Doppler signal which is given by the frequency difference of the beams.

Since the phase of the Doppler signal is related to the particle's

position particle displacement is reflected by a change of the phase of the scattered light. To improve statistics amplitude weighting of the measured phase differences was used. This allows the registration of very small particle displacements otherwise overwhelmed by random Brownian motion. The advantage is that frequency-spectra of particle translation induced by DP or TWDP can be registered at low field strengths. In a first application PALS was used to measure TWDP-induced particle pumping within an optical ultramicro-chamber. The frequency, field strength and medium conductivity dependence of pumping was characterized. The translation of particles with sizes smaller than 15 nm in diameter could clearly be detected. Our method overcomes the limitation of microscopic methods and allows computerization of the measuring procedure.

## 717.F3 ENVIRONMENTAL EFFECTS ON THE PHOTONICS OF ADSORBED FLUORESCENT PROBES

Eremenko A.M., Kikteva T.A.

*Institute of Surface Chemistry, National Ukrainian Academy of Science, Kiev, Ukraine*

Silica and silica minerals are widely used materials in the environment, and a lot of organic pollutants are often adsorbed on their surfaces. Recently, a growing interest has developed in photoinduced processes of organic adsorbates on silica, in particular photoinduced electron transfer and subsequent reactions of radical species. In this paper bimolecular excited complex between Pyrene (Py) and N, NDimethylaniline (DMA) was chose as a model compound, for elucidation of effects of polar additions on photophysical and photochemical perturbations on silica surface. It is well-known that the solvent polarity has a significant influence on the processes of charge transfer in excited state and charge separation. When polarity of medium is high than dissociation on solvent-separated ion-radicals take the important meaning as one from the non-radiative deactivation ways of high polar excited complexes. Photoinduced electron transfer between Py and the porous silica gel matrix results in the formation of the Py cation a separated

electron. High temperature pretreatment of silica increases the stability and life time of the Py cation. Charge separation is increased by removing the silanol groups from the surface adsorption sites and appearance of electron-deficient defective sites in silica structure.

A reaction of exciplex formation (Py...DMA)\* on the surface of dehydrated porous silica fractosil, silochrom-120, porous glass, non-porous aerosil proceeds very effectively starting from concentration of DMA from  $10^{-6}$  and to  $10^{-4}$  M/g DMA, when Py concentration is  $10^{-7}$  M/g. Maximum of exciplex emission is 500 nm. In the presence of polar coadsorbates, intensive luminescence of PY-DMA exciplex adsorbed on the surfaces of above mentioned carriers is observed during 3 - 4 minutes after beginning of registration. After this a spectrum of exciplex emission disappears and a new broad and hypsochromic shifted luminescence spectrum with maximum 440 nm appears. Non-reversible changes of adsorbates occur. Non-fluorescent yellow-colored product of photochemical reaction on the surface is formed. Formation of three fluorescent species and non-fluorescent product of photochemical reaction is established. Photochemical behavior both of Py and exciplex is strongly dependent on the purity of samples. Under action of pulse laser irradiation, ion-radicals of Py anion-radical, DMA cation-radical and Py triplet appeared on the silica surface after addition of water or methanol vapors to the system. When Py and DMA are solubilized in aqueous micelles of TX-100 and then adsorbed on aerosil surface, the influence of the surface on the photoreaction kinetics is negligible. A removal of water from the above system leads to a suppression of the photoreaction. Appearance of an abnormally long life time of Py may be explained by a rearrangement of an adsorption layer, micelles degradation and encapsulation of fluorophore. A course of photoreaction of electron transfer between components and the kinetics characteristics of decay are determined by the adsorption conditions. Processes of sol-gel-xerogel transformation in an aqueous-micellar medium of aerosil in the presence of Py fluorophore lead to an emergence of abnormal long decay time due to its encapsulation in the matrix and inaccessibility for quencher molecules.

## 718.F3

### MEASUREMENT OF INHERENT PARTICLE PROPERTIES BY DYNAMIC LIGHT SCATTERING

Jan Gimsa, Bernhard Prüger, Peter Eppman

*Inst. Biology, Humboldt-Univ., Invalidenstr. 42, D-101 15 Berlin, Germany*

Common dynamic light scattering (DLS) methods determine the size and  $\zeta$ -potential of particles by analyzing the motion resulting from thermal noise or electrophoretic force. Radio-frequency fields may also induce forces on particles which evolve from the interaction of induced polarization charges with the applied field. Particle polarization depends on field frequency, as well as on the dielectric properties of the suspension medium and the internal particle structures. Depending on the field characteristics, translation (dielectrophoresis, DP; traveling wave dielectrophoresis, TWDP) or rotation (electrorotation, ER) of particles can be induced. Common dielectric particle spectroscopy methods microscopically analyze the frequency behavior of the induced motion to obtain information on the particles' internal structures. We propose new techniques that apply DLS for observation of the field induced particle motion.

Phase analysis light scattering (PALS) allows detection of extremely slow translational particle motion. The measuring volume of PALS is defined by the crossing region of two laser-beams of an extremely low frequency difference (2 kHz). By comparison of the phase behavior of the scattered light intensity with an electronic phase reference, translational particle motion can be detected. The high sensitivity allows to record frequency-spectra of particle translation induced by DP or TWDP at low field strengths. In a first application PALS was used to measure TWDP-induced particle pumping within an optical ultramicro-chamber. The frequency, field strength and medium conductivity dependence of pumping was characterized. Particles smaller than 15 nm in diameter could clearly be detected.

Also, we developed electrorotational light scattering (ERLS) to measure ER in a particle ensemble. A special optical ER-chamber was developed for a homodyne DLS setup. Human red blood cells were used as test particles. Induced particle rotation was extracted from the initial decorrelation of the intensity autocorrelation function (ACF). ER led to an additional decorrelation of the ACF. Criteria for deduction of ERLS-frequency spectra were found. Although, the absolute rotation speed and the rotation sense are not yet directly accessible, ERLS allowed to determine the cell's membrane capacitance and internal conductivity.

By eliminating the tedious microscopic measurements our new methods offer computerized, statistically significant measurements of dielectric particle properties also at particle sizes below the reach of microscopic methods.

## 719.F3

### EFFECT OF PORE SIZE ON THE STATE OF WATER ADSORBED ON SILICA

Hideaki Hamano, Yasushige Kuroda, Mahiko Nagao

Faculty of Science, Okayama university, Okayama, Japan

Water adsorption on metal oxide surfaces has been a subject under study for many years, because of its fundamental significance to various technological processes. Interfacial water has properties that differ considerably from those of bulk water. The properties of water in small pores are also influenced and, for example, the freezing point of adsorbed water layers is shifted to lower temperatures. However, the dynamic properties of water in pores have scarcely been studied. In this study, we prepare silica samples that have different pore sizes and aim to know the dynamic properties of adsorbed water on silica samples through dielectric measurement.

Silica samples were prepared through the reaction of sodium silicate with sulfuric acid. Dinitrogen and water adsorption isotherms were measured by using a conventional volumetric apparatus at 77 K and 298 K, respectively. Dielectric measurements were carried out by the same procedures previously described.<sup>1)</sup>

Two dielectric relaxations were observed at around 1 kHz and 200 kHz as a result of dielectric measurement at 298 K and at the coverage ( $\theta$ ) of 1.2 for the  $\text{SiO}_2\text{-H}_2\text{O}$  system in which silica sample has a pore-size ( $d$ : diameter) of 7.0 nm. Both relaxations can be interpreted to the interfacial polarization due to heterogeneity of the system. It was also found that the additional dielectric relaxation appears at around 200 kHz and at 179 K and that the arc length of Cole-Cole plots for this relaxation increases with increasing coverages. Based on these data, the latter relaxation is assigned to the orientational polarization due to physisorbed water molecules. An activation energy for this relaxation was estimated to 40 kJ/mol from the plot of  $\log f_m$  ( $f_m$ : characteristic frequency) vs.  $1/T$ . Taking account of the values of  $f_m$  and of this activation energy, it should be noted that physisorbed water molecules ( $\theta \leq 2$ ) does not freeze even at lower temperatures of 149 K and that the state of these molecules are intermediate between that of ice and of liquid water. Figure 1 (dielectric loss against frequency) shows the dielectric relaxation curves due to the orientational polarization of physisorbed water molecules on non-porous  $\text{Y}_2\text{O}_3$  sample and on  $\text{SiO}_2$  having pore sizes of 3.4 and 7.0 nm. This figure shows the  $f_m$  value for  $\text{SiO}_2\text{-H}_2\text{O}$  system is lower than that for  $\text{Y}_2\text{O}_3\text{-H}_2\text{O}$  system, indicating water molecules physisorbed on  $\text{SiO}_2$  sample is less mobile than those on  $\text{Y}_2\text{O}_3$  surface. It is also found that water molecules physisorbed in the small pore size is less mobile than those in the large one by comparing the  $f_m$  values in the two  $\text{SiO}_2\text{-H}_2\text{O}$  systems. On the basis of dielectric and infrared spectroscopic data, the dynamic properties and the adsorption model for water physisorbed on solid surface will be discussed.

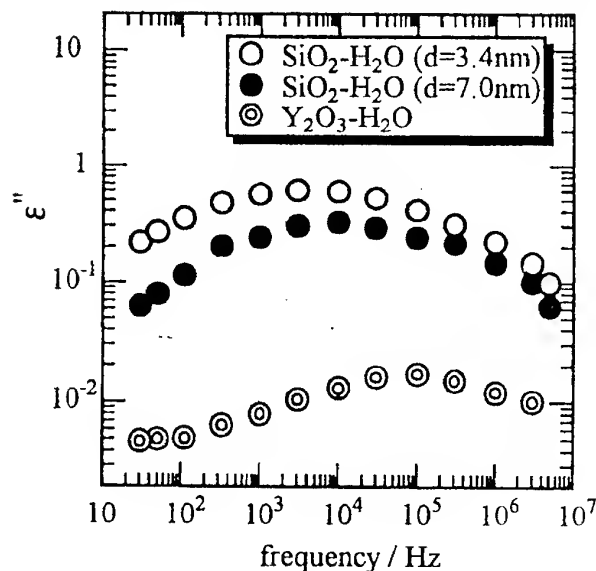


Figure 1. Dielectric loss- $f$  curves for metal oxides- $\text{H}_2\text{O}$  systems ( $\theta=1$ , 159 K).

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## 720.F3

STUDY ON THE ADSORBED STATE OF WATER  
TWO-DIMENSIONALLY CONDENSED ON NaF SURFACEToshinori Mori<sup>1</sup>, Yasushige Kuroda<sup>1</sup>, Yuzo Yoshikawa<sup>1</sup>, Shigeharu Kittaka<sup>3</sup> and Mahiko Nagao<sup>2</sup><sup>1</sup>Dept. of Chemistry and <sup>2</sup>Research Laboratory for Surface Science, Faculty of Science,  
Okayama University, Tsushima-naka, Okayama 700, Japan<sup>3</sup>Dept. of Chemistry, Faculty of Science, Okayama Science University, Ridai-cho, Okayama 700, Japan

A study on the properties of water chemisorbed on such solid surfaces as metals, semiconductors, and oxides has drawn a great deal of attention in view of the significant effect of adsorbed water on the surface properties of solid. However, little is known on the state of physisorbed water, though it exists invariably on the solid surfaces. It is commonly believed that the structure and dynamics of water are modified by the state of solid surfaces, both by a change of the hydrogen bonding and by a modification of the molecular motion. In regard to the physisorbed water modified by the surface, we have found the step in the adsorption isotherm of water on some kinds of oxides or ionic compounds, and ascribed this phenomenon to the two-dimensional condensation of water on the homogeneous solid surfaces.

In this study, the state of water two-dimensionally condensed on the NaF surface was examined through the measurements of dielectric losses and infrared spectra, and by the simulation method.

Figure 1 shows the adsorption isotherm of water on NaF at 298 K, in which a distinct step can be observed. This step is apparently caused by the two-dimensional condensation of adsorbed water molecules through the lateral interaction on the homogeneous NaF surface. Such interpretation was supported by the fact that Kr adsorption, which is useful in evaluating a surface homogeneity of solid, also gave a distinguished step in the isotherm.

Figure 2 represents the relationship between the dielectric loss and frequency for the NaF-H<sub>2</sub>O system (at the coverage of 0.8 and at 273 K). A large relaxation is observed at 5 Hz, which can be ascribed to the interfacial polarization caused by the heterogeneity of the system. Another relaxation is also observed as a shoulder at 330 Hz, and it can be assigned to the orientational polarization of adsorbed water molecules. Therefore, it may be said that the adsorbed water on NaF at 273 K, which is lower than the two-dimensional critical temperature of water, are in a solid-like state. The IR spectra gave a broad band at around 3200 cm<sup>-1</sup>, supporting the above interpretation. In addition, we tried to build a model for the adsorbed water molecules on NaF at 273 K by means of Monte-Carlo simulation technique. As a result, it was suggested that the phase transition takes place in the vicinity of monolayer coverage to form a stable hydrogen-bonded layer, probably forming an ordered two dimensional "ice-like" structure.

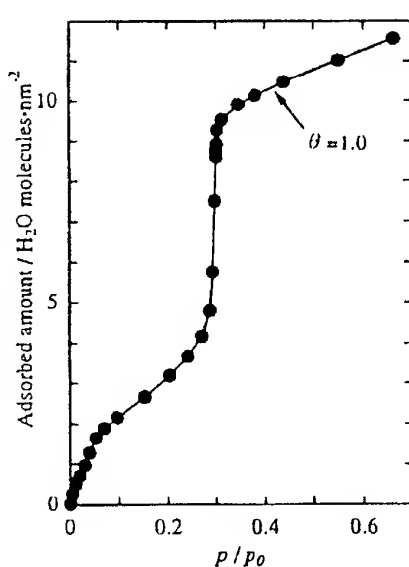
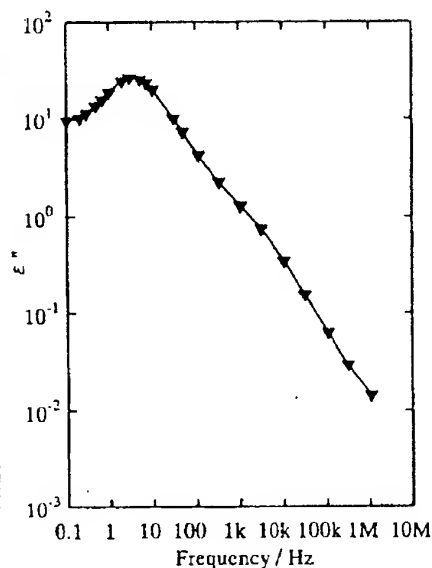


Fig 1. Adsorption isotherm of water on NaF at 298K

Fig 2. Dependence of dielectric loss ( $\epsilon''$ ) on frequency for adsorbed water on NaF

## 721.F3

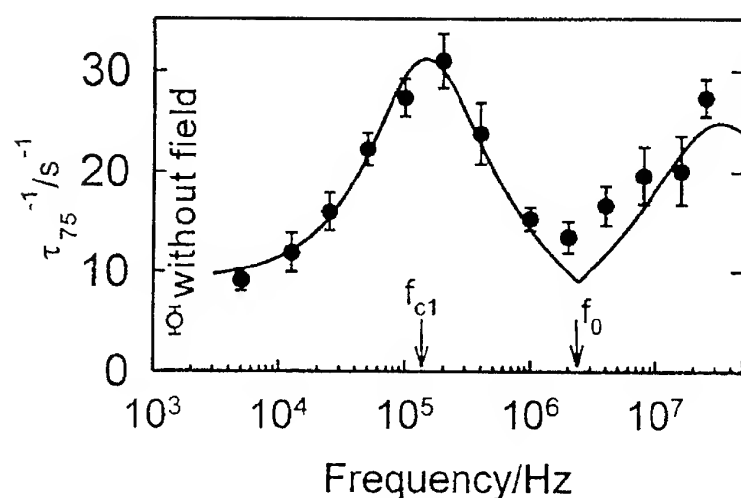
# INHERENT PARTICLE PROPERTIES MEASURED BY ELECTROROTATIONAL LIGHT SCATTERING (ERLS)

Bernhard Prüger, Peter Eppmann, Jan Gimsa

*Inst. Biology, Humboldt-Univ., Invalidenstr. 42, D-10115 Berlin, Germany*

Microscopic electrorotation (ER) is a useful method for the determination of dielectric particle properties. It analyzes the frequency dependence of particle rotation induced by a rotating electric field. Any dispersion process is reflected as a maximum of particle rotation and characteristic relaxation times of such processes can be directly determined from ER peak frequencies. Also, dielectric particle properties can be recalculated by applying an appropriate dielectric particle model. To overcome the tedious microscopic measurements, we developed electrorotational light scattering (ERLS). The method detects ER from a particle ensemble in a special optical ER-chamber. A homodyne dynamic light scattering (DLS) setup is used. Human red blood cells were used as test particles because their dielectric properties are well known. At a medium conductivity of 10 mS/m these cells exhibit a membrane dispersion peak at a frequency of

$f_{c1}=150$  kHz. In our chamber a peak rotation of  $2\text{ s}^{-1}$  was induced at a field strength of 12 kV/m. This rotation led to a faster decorrelation of the intensity autocorrelation function (ACF) which was about 10 times steeper than that of the field free control. We found that the initial decorrelation of the ACF reflects the ER-induced particle rotation. Applying a simple optical particle model ER frequency spectra can be extracted when the inverse of the time necessary for the ACF to decay to 75% of the initial level ( $1/\tau_{75}$ ) was used as a measure for the rotation speed (figure). Each point presents 6 ACF-measurements. The solid line is the comparison to the theoretical



ERLS-spectrum calculated from the dielectric and a simple optical cell model. Thus from ERLS-measurements membrane capacitance and internal conductivity could be calculated. Also, changes of the dielectric cell properties induced by the ionophore nystatin were monitored by a characteristic change of  $f_{c1}$ . Recalculation revealed that the ionophore induced a decrease of the internal conductivity. Although the absolute rotation speed and the rotation sense are not yet directly accessible, ERLS offers computerized, statistically significant measurements of dielectric particle properties which are especially suitable for non-biological applications, e. g. the study of colloidal particles.

**722.G1 FRAP MEASUREMENTS IN POLYELECTROLYTE MULTILAYERS****Mark Auch, Birgit Fischer and Helmuth Möhwald***Max-Planck-Institut für Kolloid- und Grenzflächenforschung, 12489 Berlin, Germany*

The diffusion of probes with different charges and of different sizes in Polyelectrolyte multilayers using the technique of Fluorescence Recovery after Photobleaching (FRAP) is of importance from a scientific as well as applicational point of view.

In order to understand the processes, we prepared films of defined thicknesses and ionic strengths by consecutive electrostatic adsorption of polyelectrolytes. Diffusion is measured by fluorescence recovery after photobleaching, which has the advantage that the original fluorophore concentration is not relevant for the measurement, since only the decay of the pattern is recorded.

We find a drastic dependence on the type of probe and on the hydration state of the film. This will be discussed in a model, considering a locally heterogeneous mobility of the film.

**723.G1 PROPAGATION OF PHOTOINDUCED SURFACE PRESSURE  
PERTURBATION ALONG A MIXED BENZOSPIROPYRAN - OCTADECANOL MONOLAYER****K. Balashev<sup>1</sup>, I. Panaiotov<sup>1</sup>, J.E. Proust<sup>2</sup>**<sup>1</sup>*Biophysical Chemistry Laboratory, University of Sofia, J. Bourchier str.1, 1126 Sofia, Bulgaria*<sup>2</sup>*Pharmacie Galénique et Biophysique Pharmaceutique, Faculté de Pharmacie,  
16 Bd Daviers, 49100 Angers, France*

The state and the elastic dilatational properties of a mixed spiropyran (with attached hydrocarbon chain) - octadecanol (1:5, mol/mol) spread monolayer were studied. A localized photochemical excitation was used to generate dilatational motion along the elastic monolayer. The surface pressure variations at various distances from the photoexcited region were measured. The experimental results are in quantitative agreement with a theoretical model taking into account the rheological properties of the interface and the liquid substrate as well as the rate constant for the photochemical process.

**724.G1 INTERFACIAL DIFFUSION CONTROLLED REACTIONS WITH  
TIME VARYING ADSORBING DOMAINS****M. Baldo<sup>1</sup>, A. Grassi<sup>2</sup>, G.M. Lombardo<sup>2</sup> and A. Raudino<sup>3</sup>**<sup>1</sup>*Dipartimento di Fisica, Università di Catania, C.so Italia 57, 95125 Catania, Italy*<sup>2</sup>*Dipart. di Scienze Chimiche, Facoltà di Farmacia, Univ. di Catania, V.le A. Doria 6, 95125 Catania, Italy*<sup>3</sup>*Dipartimento di Scienze Chimiche, Università di Catania, V.le A. Doria 6, 95125 Catania, Italy*

A theoretical study for the diffusional crossing of a tracer through a membrane, where the size of the adsorbing domain (receptor) is time-dependent, is presented [1]. A periodic array of adsorbing and reflecting domains upon the membrane surface was assumed. This model is described by a time-dependent diffusion equation with mixed boundary conditions, where the boundaries are themselves varying with time. Both analytical and numerical methods were employed by order to calculate the total flux of a tracer across the membrane as function of the oscillation frequency ( $\omega$ ) and amplitude ( $\epsilon$ ) of the receptor site. At fixed  $\epsilon$ , the results evidence an increasing of the adsorption rate with frequency, reaching a plateau at very high values of  $\omega$ . The space and time behaviour of the diffusing tracer concentration was analysed, showing dephasing effects at high  $\omega$  which are common to many non-linear systems where the dynamic response becomes time-independent in the high frequency limit. This approach has been used to explain the anomalous effect of an oscillating electric field on the permeability of lipid membranes which exhibits a maximum in the micro-wave region.



**725.G1****DYNAMICAL PROPERTIES AT LIQUID LIQUID INTERFACE,  
USING AN AUTOMATED PENDANT DROP TENSIO METER****A. Bois<sup>1</sup>, G. Faour<sup>1</sup>, I. Panaiotov<sup>2</sup>, K. Balashev<sup>2</sup>, J. Proust<sup>3</sup>, F. Boury<sup>3</sup>**<sup>1</sup>*LOE, Université de Toulon et du Var, Toulon, France*<sup>2</sup>*BPCL, University of Sofia, Sofia, Bulgaria*<sup>3</sup>*PGBP, Université d'Angers, Angers, France*

The use of a real time automated pendant drop tensiometer with interfacial area and interfacial tension control capabilities allows to study the dynamical properties of adsorbed films at liquid liquid interfaces as monolayers can be studied at gas liquid interfaces using a Langmuir trough.

From a digitized profile of a pendant drop and the use of an integrated form of Laplace equation, the interfacial tension can be determined with an accuracy of 0.2%. As this tensiometer allows several measurements per seconds (3 to 5), it is possible to control the interfacial area or the interfacial tension during an experiment. Thus, the interfacial area or interfacial tension can be maintained constant during an adsorption kinetics as well as constraints can be applied to the adsorbed layer to determine the dynamical properties of the adsorbed layer.

Different applications to the study of adsorbed polymers and proteins at liquid liquid interfaces are presented: adsorption kinetics (by fast compressions and expansions the number of adsorbed molecules can be determined through the compressibility), dynamical properties of the Marangoni effect (dilatational elasticity and viscosity of adsorbed layers), chemical reaction (reticulation of a polymer at the interface) and adsorption kinetics at constant interfacial tension (the change in interfacial area corresponds directly to the number of adsorbed molecules).

**726.G1****NONLINEAR STABILITY OF THIN LIQUID FILM WITH  
SURFACE CHEMICAL REACTIONS****D. Gallez, A. De Wit and M. Kaufman***Université Libre de Bruxelles, Faculté des Sciences Campus Plaine, CP231, 1050 Bruxelles, Belgium*

The influence of a chemical reaction on the dynamical behaviour of a thin liquid film is of significant importance in many engineering and biological applications. The dynamics of a thin liquid film on a solid substrate is followed until film rupture or formation of local contacts (periodic patterns). Previous work [1,2] has assessed the role of the geometry of the film and of the dynamics of the surfactants.

A surface chemical reaction between insoluble surfactant molecules (receptors) on the free surface of the film and binding sites on the solid substrate is now considered [3]. Asymptotic expansion of the equations for fluid motion with van der Waals, capillary and Marangoni forces allows to obtain a model with 3 non-linear evolution equations describing the dynamics of the surface deformation, and the kinetics of free and bound receptors. Chemical and hydrodynamic instabilities are predicted and simulated numerically with different stability regimes. For a simple surface reaction, the concentration of receptors follows the deformation of the surface; for a non-linear surface reaction (affinity enhanced at small distances), a clustering of receptors is observed at the local points of contacts. When the Marangoni coupling is increased, a completely new regime is obtained, where the receptor concentration oscillates, delaying the rupture (or contact) time by several orders of magnitude. A critical density of binding sites is also necessary to observe this time delay.

Possible application to bioadhesion will be discussed [4].

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## 727.G1 MASS TRANSPORT MODEL AT SOLID/SOLID/FLUID INTERFACES

V.V. Gusarov<sup>1</sup>, F.K. Egorov<sup>2</sup>

<sup>1</sup>St.-Petersburg State Technological Institute (Technical University), St.-Petersburg, Russia, USSR

<sup>2</sup>AO Bang & Bonsomer, St.Petersburg, Russia.

The experimental investigation of transformations and mass transport of solid phases components in the systems  $\text{BeO-FeO}_{1.5}$ ,  $\text{AlO}_{1.5}\text{-FeO}_{1.5}$ ,  $\text{MgO-FeO}_{1.5}$ , and  $\text{SiO}_2\text{-FeO}_{1.5}$  in air in the temperature range 1000-1600 K was made. The quantities of iron oxide in the bulk of crystals and in the interfaces was defined by Mossbauer spectroscopy method. Evolution of the fractional contribution of various iron states was presented as a function of the annealing temperature and annealing time. The kinetic analysis showed, very low rate of mass transport processes in the systems for the temperature less than  $T_{m2n}$  and high rate of ones for the temperature greater than  $T_{m2n}$ ; where  $T_{m2n}$  is the melting point for the interface.

Theoretical analysis is showed that the diffusion models can not describe high rate of mass transport at the interfaces for the temperature range  $T > T_{m2n}$ . For this temperature range mass transport processes was described by the model of creeping flow of liquid-like interface of finite width. The kinetic equation for the high-temperature mass transport process was proposed. It can be expressed as follows:

$$\tau = (S_{\text{solid1/fluid}} / S_{\text{solid1/solid2}}) h / (\mu f),$$

where  $\tau$  is a time of flow,  $S_{\text{solid1/fluid}}$  and  $S_{\text{solid1/solid2}}$  are a surfaces squares of solid1/fluid interface and solid1/solid2 interface (see fig. 1),  $h$  and  $\mu$  are a thickness and a viscosity of a liquid-like interface of finite width, and  $f$  is a surface tension.

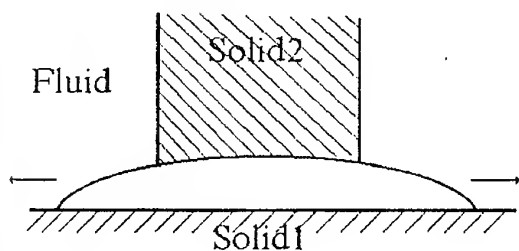


Fig. 1.-Geometrical configuration of the system.

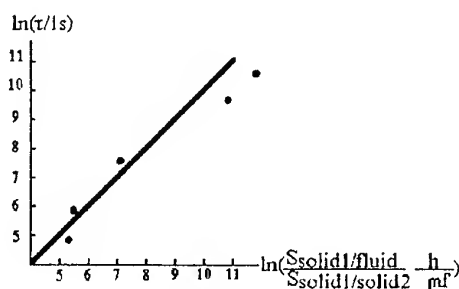


Fig.2.-Time of flow (theoretical values and experimental results)

The model of creeping flow of liquid-like interface of finite width was supported by the experimental results (see fig. 2).

## 728.G1 UNUSUAL PROPERTIES OF SOLID/SOLID INTERFACE FLOW

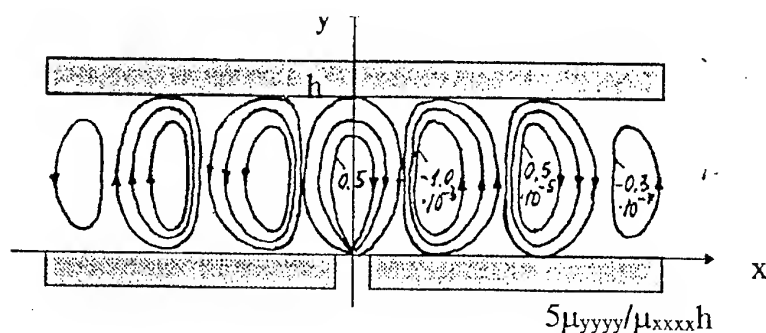
V.V. Gusarov<sup>1</sup>, I.Yu. Popov<sup>2</sup>

<sup>1</sup>St.-Petersburg State Technological Institute (Technical University), St.-Petersburg, Russia, USSR.

<sup>2</sup>Leningrad Institute of Fine Mechanics and Optics, St. -Petersburg, Russia, USSR

In contrast to the ordinary liquids, the properties of the liquid-like interfaces of polycrystalline systems are anisotropic and non-homogeneous ones. The components of the viscosity tensor differs drastically ( $\mu_{yyyy} > \mu_{xxxx}$ , see figure ) due to the great variation of the atoms (or ions) mobilities in respect to different directions. It is known that the viscosity varies rapidly in the close proximity of the boundary only. We assume that the interface thickness is so big that one can use hard wall approximation for this narrow domain with extremely great viscosity. 2D steady flow in a neighbourhood of triple grain boundaries is considered. This transport process may be considered as a creeping flow because the corresponding Reynolds number is extremely small. As a result, the Navier-Stokes equations reduce to the biharmonic one for stream function  $\varphi$ , having the following relation with the velocity:  $v_1 = \partial\varphi/\partial x$ ,  $v_2 = -\mu_{xxxx}/\mu_{yyyy} \partial\varphi/\partial y$ , where  $\mu_{xxxx}$ ,  $\mu_{yyyy}$ , are constants. The function  $\varphi$  satisfies the Dirichlet boundary condition.

The use of zero-range interaction approach (see, e.g. [1]) based on the theory of self-adjoint extensions of symmetric operators allows us to get the solution in an explicit form. The picture of the flow is shown on the figure. One can see that eddies exist.



The existence of eddies in the flow leads to the chemical separation of atoms (ions) of different types in the interface. This chemical structures appear due to the flow only. Eddies structure of the flow may be also one of the causes of the effect of super plasticity in polycrystalline systems under high temperatures. The effects were considered in [2] for a more simple case of isotropic liquid.

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## 729.G1 TEMPERATURE EVOLUTION IN A CONVECTIVE-DIFFUSIVE LATTICE-GAS MODEL FOR THERMOCAPILLARY FLOWS

Adil A. Khan<sup>1</sup>, Yonathan Shapir<sup>1</sup> and Yitzhak Shnidman<sup>2</sup>

<sup>1</sup>University of Rochester, Rochester, New York 14627, USA

<sup>2</sup>Eastman Kodak Company, Rochester, New York 14650, USA

We report a nonisothermal generalization of an earlier convective-diffusive lattice-gas model for microcapillary flows. This is achieved by incorporating heat transport and imposing local conservation of energy, as well as of species numbers and of momentum. Within a mean-field approximation, we derive a set of difference equations describing the time evolution in discrete space-time of the temperature field, as well as of the local species and momentum densities. The evolution equations consist of alternating convective and diffusive steps, subject to the conservation laws, and to appropriate boundary and initial conditions.

Between diffusive steps, the temperature, species densities and momentum fields are convected by a local velocity, corresponding to the mean velocity of the cage of neighboring molecules. Diffusion of the species and momentum densities proceeds by hops from occupied to adjacent vacant cages. In contrast, the temperature, which is a measure of the width of the local Maxwell-Boltzmann molecular velocity distribution within the cage frame, diffuses primarily by thermal energy exchange between adjacent occupied cages. The capabilities of the model are illustrated by numerical application to a number of thermocapillary phenomena.

## 730.G1 FORMATION OF HIGHLY DISPERSED SILICA NANOPARTICLES. SUPERCLUSTER APPROACH: QUANTUM-CHEMICAL MODELLING AND VIBRATIONAL SPECTRA VERIFICATION.

V.D. Khavryutchenko<sup>1,2</sup>, E.A. Nikitina<sup>3</sup>, W.H. Barthel<sup>4</sup> and E.F. Sheka<sup>5</sup>

<sup>1</sup>Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Kiev, 252028 Ukraine

<sup>2</sup>Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, 141980 Russia

<sup>3</sup>Institute of Applied Mechanics, RAS, Leninsky prospekt 32A, Moscow, 117334 Russia

<sup>4</sup>Wacker-Chemie GmbH, Werk Burghausen, D-84480 Burghausen, Germany

<sup>5</sup>Russian Peoples' Friendship Univ., General Physics Dept., ul. Ordjonikidze 3, Moscow, 117302 Russia

The formation of highly dispersed silica nanoparticles was investigated by a supercluster approach in quantum-chemistry. Using the semiempirical methods AM1 and PM3 we designed supercluster models of

silica nanoparticles based on cristobalite-like arranged clusters of silicon dioxide units, surface terminated with hydroxyl groups. The clusters contain from 54 up to more than 250 atoms and show sizes up to 3 - 4 nm. After full space structure optimization an amorphous state was achieved, characterized by a broad distribution of Si-O-Si bond angles. The results from AM1 seems to represent the high temperature modification of a cristobalite-like structure, whereas the PM3 approach may describe the low temperature modification of a cristobalite-like structure. Force field and dipol moment derivatives are provided, additionally. The infrared spectra (IR) and neutron inelastic scattering spectra (INS) of the superclusters have been calculated and show a good agreement with experimental data. Spectral details observed during the modelling steps towards silica clusters reveal to describe real particle-particle interactions. For some series of the silica cluster-cluster systems we performed the full space structure optimization and vibrational spectra calculation. The pathway of cluster interactions have been animated as movies. The calculated vibrational spectra provide informations to understand the particle-particle interactions and their influence on vibrational spectra, IR and INS. The interactions between silica clusters may be separated into long distance dipol-dipol interactions and short distance H-bond interactions. As well known, the heating treatment of highly dispersed silica particles lead to the condensation of hydroxyl groups and the formation of siloxane bonds. We realized some models of this process which lead to the formation of superclusters with sizes up to 5 nm and which are comparable to real substances. We propose that these models are able to represent the formation of fumed silica in the flame, and also its structure and properties. Details of cluster structures and their vibrational spectra (IR and INS) will be presented and discussed.

### 731.G1 THE FAST PROJECT: STUDY OF DYNAMIC ADSORPTION PROCESSES IN MICROGRAVITY

L. Liggieri<sup>1</sup>, M. Ferrari<sup>1</sup>, F. Ravera<sup>1</sup>, R. Miller<sup>2</sup>, G. Loglio<sup>3</sup> and A. Passerone<sup>1</sup>

<sup>1</sup>*Istituto di Chimica Fisica Applicata dei Materiali - CNR, Genoa, Italy*

<sup>2</sup>*Max Plank Institut für Kolloid und Grenzflächenforschung, Berlin, Germany*

<sup>3</sup>*Dipartimento di Chimica Organica-Università di Firenze, Florence, Italy*

An ideal environment for all experiments dealing with dynamic adsorption processes for which diffusion plays a fundamental role is today available on space platforms where the conditions of weightlessness, or microgravity, are achieved. Indeed the large attenuation of convective fluxes, and the possibility to operate on spherical surfaces represent a mandatory requirement to test theoretical approaches to adsorption kinetics and diffusion avoiding superposition of gravity-driven convection effects, and to explore the behaviour of systems under higher frequency interface area excitations.

A Facility for Adsorption and Surface Tension studies (FAST) has been successfully proposed in the framework of the European Space Agency precursor flights activities for the International Space Station Columbus. In the FAST experimental module there are three kind of experiments, scheduled for a first flight on 1998, aimed at studying dynamic phenomena at liquid-liquid and liquid-gas interfaces (evaluation of adsorption kinetics, dynamic surface tension, interfacial dilational modulus, surface viscosity etc.) under microgravity conditions. The three experiments proposed use the same experimental facility and operate with the same chemical components, in order to get a complete evaluation of the physicochemical parameters governing the dynamic behaviour.

In this work the principles of the Capillary Pressure Tensiometer, which is the core of the facility, and the main lines of the three selected experiments for this first flight are summarised.

### 732.G1 DYNAMICS OF ADSORPTION OF SOLUBLE SURFACTANTS AT LIQUID INTERFACE: MIXED KINETICS AND TRANSFER ACROSS THE INTERFACE

L. Liggieri, M. Ferrari, F. Ravera and A. Passerone

*Istituto di Chimica Fisica Applicata dei Materiali, CNR, Genova, Italy.*

When the dynamics of adsorption of non ionic surfactant at liquid-liquid or liquid-air surfaces is considered, in some cases, the classical diffusion controlled model is not adequate and the system presents a mixed mechanism of adsorption in which diffusion, transfer kinetics and adsorption barrier are important.

A diffusion based approach to describe this dynamic process<sup>1</sup> is applied here to interpret experimental data of dynamic interfacial tension for systems that seem do not follow the diffusion controlled adsorption mechanism. Moreover, in order to describe adsorption kinetics at water-oil interfaces one needs to take into consideration the transfer from one phase to the other one. In fact as experimentally shown<sup>2</sup> the partition coefficient in water-oil of most surfactants presents a solubility in both liquids which is not negligible when adsorption kinetics processes are under study.

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## 733.G1

### FILM BOILING OF A DROPLET ON A CURVED SURFACE

M. Lin<sup>1</sup>, J. Pantaloni<sup>1</sup>, A. Bois<sup>2</sup>, H. Gouin<sup>3</sup>

<sup>1</sup>IUSTI, Université de Provence, Marseille, France

<sup>2</sup>LOE, Université de Toulon et du Var, Toulon, France

<sup>3</sup>LMMT, Université d'Aix-Marseille II, Marseille, France

Water or alcohol droplets deposited on a curved heating surface at a temperature greater than the boiling temperature of the liquid, present oscillations of their surface until they completely evaporate.

The life time of these droplets are studied as function of the heating temperature, the difference between the temperatures of the droplet and the heater, and the initial volume of the droplet. For temperatures greater than the temperature of the Leidenfrost point, which corresponds to the maximum life time as a function of the heater temperature, a good correlation with the overheated steam thermal conductivity coefficient is found.

The oscillating modes of the droplets depend on the curvature of the heating surface, the heating temperature, and the volume of the droplet. During an experiment, different modes can be observed as the volume of the droplet decreases.

## 734.G1

### MICROSCOPIC OBSERVATIONS OF WALL EFFECTS IN COLLOIDAL SUSPENSIONS

Holger Manteufel\* and Heiner Versmold

Institut für Physikalische Chemie, RWTH, D-52062, Aachen, Germany

The properties of colloidal suspensions differ slightly between their boundary walls and the bulk. We describe in our work the influence of a glass surface to the structure and the dynamic of a latex suspension. In the present experiments we use monodisperse distribution of 370 nm polystyrene microspheres in a mixture of H<sub>2</sub>O/D<sub>2</sub>O (50:50).

In order to study the influence of the glass plate the ionic strength and the volume fraction of the sample got varied. We use time resolved video microscopy to obtain steric and dynamic properties, such as particle number density, pair correlation function and mean square displacement. A low voltage piezoelectric translator is used for accurate positioning of the objective. Additionally a linear variable differential transformer provides a very high single step resolution (10 nm) in vertical direction at a total range of about 100  $\mu$ m.

One of the most important points of interest is the electrostatic interaction potential between the glass plate and a single microsphere  $[U(z)]$ . We determine this interaction potential through the equilibrium distribution function  $P(z) = C \exp[-U(z)/k_B T]$  at various ionic strength. In comparison with other methods we are now able to determine the interaction potential for small particle sizes. The intensity of the particles is used so far for the measurement of the vertical particle position. Another method described a scanning force microscope that allows direct measurement of the interaction potential only for very large microspheres.

The time resolved video microscopy also yields dynamic properties of the microspheres. We measured the mean square displacement to get the lateral diffusion coefficient in relation to the surface distance. Because of the hydrodynamic interactions the mobility of the particles are reduced near the glass

surface. We found an exponential relation between the lateral diffusion coefficient and the plate distance of the form:  $D_{||}=D_0e^{-z}$ .

Another subject of our work is the ordering influence of the surface. Generally it might be observed, that the ordering near to a boundry wall is higher than in the bulk. We found a layered order at the surface for a suspension, wich is isotropic liquid like ordered in the bulk. We measured the grade of the structure in relation to the volume fraction and compare the results with the phase transition in the bulk and with the theory for two dimensional melting.

## 735.G1

### DYNAMICS OF INTERFACES IN CONICAL CAPILLARIES IMMERSSED IN LIQUIDS

Nikolai P. Migoun, Alexander I. Shnipp

*Institute of Applied Physics, Belarussian Academy of Sciences, Minsk, Belarus*

The phenomenon of complete filling of one-side closed conical capillaries immersed in liquids was established in [1], but its physical nature is not entirely clear up to now [2]. The most characteristic feature of the phenomenon is the filling of a cone from both sides. Moreover, under certain conditions the cone's channel is filled mostly from the closed top.

Recently a number of experiments has been conducted to study the physical nature of the phenomenon [2]. The experiments prove that the phenomenon of two-side filling of one-side closed capillaries with liquids takes place only if a gas inside a channel is bounded by liquid surfaces of different curvatures. For instance, the cylindrical capillaries with short cone-shape closed ends are filled with the liquids as follows. During the first stage the channel is filled from both sides until the meniscus of the top's column reaches the constant value of the radius. Then the only column of a liquid is growing: the volume of the entrance's liquid column is increasing due to the diffusion of a gas from the channel's hollow towards the cone's entrance.

There are two possible physical mechanisms of the phenomenon. The first one is based on the existence of the difference between the saturated vapour pressures above the two menisci in the conical channel. It results in the evaporation of the liquid from the meniscus of smaller curvature ("classical" capillary imbibition) and the condensation of its vapour upon the meniscus of larger curvature (originally existed due to capillary condensation).

The second mechanism works if a liquid film flow occurs in the adsorption liquid layer on the channel's wall. This flow might be directed only towards the cone's top because of the decrease of the pressure in a liquid film with the increase of meniscus curvature.

Two theoretical models of the phenomenon are worked out in the study. The first is based on mathematical description of both gas-vapour diffusion and phase transition (evaporation-condensation) in the cone's channel. The second model describes theoretically a liquid film flow in the adsorption liquid layer on the channel's wall. The comparison between theoretical and experimental results has been done.

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## 736.G1

### SURFACE PROPERTIES OF METAL MODIFIED OR THERMALLY TREATED SILICAS

Slobodan K. Milonjic

*Chemical Dynamics Laboratory, Vinca Institute of Nuclear Sciences, Belgrade, Yugoslavia*

Surface properties of metal (alkali, alkaline earth, cobalt and nickel) modified and thermally treated (at 423-1223 K) silica beads were investigated by the gas-solid chromatography method. Silica beads, obtained from silica sol were characterized by their specific surface areas, crystallinity, and amount of sorbed cations. Retentions of several n-alkanes were measured in the temperature range from 330 to 500 K. As found, the applied temperature treatment does not change the crystal structure of the solids. The standard free energy of transferring a mole of vapor from the gas phase to a standard state on the surface, i.e.

adsorption energy, was calculated from the net retention volume. For n-alkanes, the free energy of adsorption is equal to its dispersive component which varies in the range from 20 to 100 mJ/m<sup>2</sup>. Both the metal modification and thermal treatment of silica lead to a decrease in the free energy of adsorption enhancing the homogeneity of the silica bead surface.

### 737.G1 ADSORPTION AND MICELLIZATION KINETICS AT THE LIQUID-GAS INTERFACE. APPLICATION OF CAPILLARY WAVES

B. A. Noskov

*Chemical Faculty, St. Petersburg State University, St. Petersburg, Russia*

The history of adsorption kinetic studies at the liquid-gas interface goes back to the very beginning of the twentieth century<sup>1</sup>. However, progress in this important field of surface science was rather slow and many authors have been discussing until now the adsorption mechanism of some basic surfactants. One of the main difficulties in these studies is related to the strong coupling of mass transport and liquid dynamics at the interface. Phenomena of this kind complicate seriously measurements of dynamic surface tension but can be excluded to a great extent if one uses only small deviations from the equilibrium. This is the principle of the methods of the relaxational spectrometry of the surface layer. Most of them, however, can be applied only in a very limited frequency range (mainly below 1 Hz). Only the application of surface waves (both transversal and longitudinal) allows us to investigate processes with characteristic times differing by several decimal orders of value. For example, capillary waves give information on the mechanism of fast adsorption processes with a characteristic time significantly less than a millisecond and on the influence of the micellization kinetics on the adsorption of conventional surfactants. Although first applications of capillary waves to the investigation of adsorption kinetics belong to the sixties<sup>2</sup>, only recent studies give evidence of the wide scope of the method<sup>3-5</sup>. In this work the results of measurements of the damping coefficient of capillary waves are compared with the theory of dynamic surface properties for solutions of non-ionic, cationic and anionic surfactants. This comparison allows us to discriminate between simple diffusional and barrier adsorption mechanisms if the surface activity of the surfactant is not too high. Otherwise the longitudinal surface waves have to be applied. Special attention is given to micellar solutions where a second maximum of the damping coefficient was discovered in the concentrational region close to the CMC. This effect was predicted by the theory of dynamic surface properties of micellar solutions and indicates at the influence of the micellization kinetics on the dynamic surface elasticity. The obtained experimental data on the wave damping are used to estimate the characteristic time of the slow stage of the micellization process. The results are in reasonable agreement with the data obtained in the course of the investigation of the bulk properties of micellar solutions.

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### 738.G1 STAGNANT SURFACE BEHAVIOUR AND ITS EFFECT ON FOAM AND FILM STABILITY

A. Prins

*Wageningen Agricultural University, Department of Food Science  
Division of Integrated Food Technology and Physics Wageningen, The Netherlands*

In studying aqueous surfactant solutions, the performance of stagnant surface layers is a well known phenomenon. A typical example of such a layer is the formation of a so-called "skin" on liquids such as beer, milk and all kind of natural waters.

From the surfactant side especially macromolecular surfactants such as proteins are found to be able to form such stagnant layers. The formation of these layers can be promoted by compressing the surface.

In order to understand the effect of these layers on the foam and film stability, the rheological properties of these layers have to be known. To this end experimental techniques have been developed. In one of these techniques the surface dilational modulus can be measured even without the use of a Wilhelmy plate. This development gets around the problem that the Wilhelmy plate disturbs these layers to such an extent that reliable surface tension measurements cannot be performed.

Elastic, visco-elastic and rupture phenomena of these layers can be measured. The consequences of these properties for foam and film stability are discussed. During foam making stagnant surfaces can effect the bubble size distribution by which also the foam stability is effected. Ostwald ripening and drainage of liquid from foam are also effected by the presence of these layers.

It is speculated that the occurrence of these stagnant layers is caused by lateral interactions between adsorbed molecules. In aqueous protein solutions it is expected that a kind of two dimensional network is formed between adsorbed protein molecules which accounts for the observed phenomena. This can explain the difference between random coil and globular proteins in their ability to form stagnant layers.

### 739.G1 EXPERIMENTAL TECHNIQUES FOR ADSORPTION PROCESSES AT LIQUID-LIQUID INTERFACES: EXPANDED DROP AND ASTRA

F. Ravera, L. Liggieri, M. Ferrari and A. Passerone

*Istituto di Chimica Fisica Applicata dei Materiali, CNR, Genova, Italy.*

In order to study the dynamic and equilibrium adsorption properties of surfactants in liquid-liquid systems, with particular attention to the transfer across the interface, experimental tools working at different time scales are necessary.

Two complementary techniques to evaluate the dynamic interfacial tension of liquid-liquid systems are presented as well as some examples of their applications. The first one, the Expanded Drop (ED) technique<sup>1</sup>, is based on the direct measurement of the capillary pressure to obtain the value of the interfacial tension through the Laplace equation. The dynamic interfacial tension is measured after a rapid expansion of a drop of one liquid inside the other one. Because this technique is applicable if the shape of this drop is quasi-spherical, liquids with similar density are used or, for the most common water-oil systems, small drops are used. The second technique is an automatic apparatus based on the drop shape method ASTRA<sup>2-3</sup> (Automatic Surface Tension Real-time Acquisition). It allows the co-ordinates of a pendant drop profile to be acquired by using a CCD camera connected to a PC Frame Grabber board. At the end of the whole acquisition, the surface tension value of each drop profile is calculated from the stored co-ordinates by fitting the Gauss-Laplace equation. An improved version of the Maze-Burnet algorithms<sup>4</sup> is used to optimise the calculation time.

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### 740.G1 ANOMALOUS SPREADING AND MOLECULAR ORIENTATION

Martin E.R. Shanahan<sup>1</sup>, Marie-Christine Houzelle<sup>2</sup>, Alain Carré<sup>2</sup>

<sup>1</sup>*Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris,*

*Centre des Matériaux P.M. Fourn, B.P. 87, 91003 EVRY Cédex, France*

<sup>2</sup>*Corning Europe Inc. 7 bis, Avenue de Valvins, 77210 AVON, France*

The spreading of a liquid on a (rigid) solid involves a dynamic energy balance in which unequibrated Young's forces lead to motion of the triple line and viscous dissipation within the liquid moderates spreading rate. For sessile drops under ideal conditions and when the contact angles,  $\theta(t)$  as a function of time  $t$  and  $\theta_0$  at equilibrium, are reasonably small ( $\leq 1$  radian), it can be shown that the spreading speed,  $U$ , should be a linear function of  $\theta(t)[\cos\theta_0 - \cos\theta(t)]$ . This has been confirmed for a model liquid, silicone oil (PDMS) on glass and two polymeric surfaces. However, some other liquids, and in particular tricresyl



phosphate (TCP), may lead to non-linear spreading behaviour on the same substrates. It is conjectured that this may be caused by the intrinsic asymmetry of the (relatively) large liquid molecules. As the liquid contacts the solid surface, an orientation of the initially randomly distributed molecules may occur in an attempt to minimise local interfacial free energy. This time-dependent process will lead to modification of the local propensity for wetting and thus invoke changes in spreading behaviour. A theory is proposed which adequately explains some aspects of the observed behaviour whilst nevertheless leaving some questions unanswered.

## 741.G1

### LECITHIN SELF-ORGANIZATION AND STRUCTURE TRANSFORMATIONS AT THE IMMISCIBLE LIQUID INTERFACE

Yurii A. Shchipunov

*Institute of Chemistry, Far East Department, Russian Academy of Sciences, 690022 Vladivostok, Russia*

Interfacial processes developed at the liquid/liquid interface after contact of a nonaqueous solution of naturally occurring lecithin with water were studied. It was established that the phospholipid self-organizes into various interfacial structures certain of which are in addition capable of undergoing spontaneous rearrangement with time. A type of structural organization and interfacial processes depends on the phospholipid concentration. At least three concentration regions can be resolved.

(i) *Very diluted solutions* (0.0001-0.001mM). An interfacial film formed in the course of spontaneous adsorption has parameters much like those of a monomolecular layer. The filling of interface corresponds to the Gibbs' theory.

(ii) *Intermediate solutions* (>0.001-10mM). Instead of the two-dimensional interfacial film, a three-dimensional one was found at the oil/water interface. There is evidence that the adsorption layer has multilayer organization resembling that of the multilamellar liquid crystals.

(iii) *Concentrated solutions* (>10mM). Interfacial processes occur not only at the interface, but they also extend over a nonaqueous layer adjacent to the interfacial boundary. Separation of a liquid phase and formation of a jelly-like phase and solid precipitate were observed.

The features of self-organization of lecithin and interfacial processes at the immiscible liquid interface are mainly caused by phospholipid hydration. With adding up to 30 water molecules, a lecithin molecule is rendered less soluble owing to a significant increase in its hydrophilicity. This leads to a gradual accumulation of phospholipid at the oil/water interface, resulting in the transformation of two-dimensional film into a three-dimensional one. In concentrated solutions, there is a possibility of further complication of phase behavior. Some bulky processes are induced by trace amounts of water that transfers into the nonaqueous solution. It was established that the initial spherical reverse micelles transform into rod-shaped ones, and then into polymer-like aggregates making up a jelly-like phase. The latter separates into a diluted solution and a compact gel or solid precipitate as soon as the water amount exceeds a critical value (about 2-3 water molecules per lecithin molecule). The phase separation terminates the rearrangement of lecithin structures. As this takes place, a diluted solution, which is released in the neighborhood of the oil/water interface, rises to the surface and a compact gel or precipitate is incorporated into the interfacial film.

## 742.G1

### LINEAR SURFACE WAVES ON LIQUID-VAPOUR INTERFACE: ROLE OF THE PERMANENT SURFACE DIPOLE MOMENT

R. Tsekov<sup>1,2</sup>, H.J. Schulze<sup>2</sup>, B. Radoev<sup>1</sup> and E. Manev<sup>1</sup>

<sup>1</sup>*Department of Physical Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

<sup>2</sup>*Research Group at the Freiberg University of Mining and Technology, Max-Planck-Institute for Colloids and Interfaces, D-09599 Freiberg, Germany*

The role of a permanent dipole moment generated by adsorption of polar surfactants in the dynamics of surface waves is studied theoretically. An important step in the present work is the description of the interfacial electrostatics by a surface (two dimensional) Maxwell equation. The effects of polarisation of the considered dielectric medium are neglected in the performed linear analysis; i.e. there are no Maxwell tensors in the stress balances. However, there are linear effects of the surface dipole moment on the mass

and momentum balances at the interface. The dispersion relation of the surface waves is derived. Due to the surface dipole moment surface elasticity is suppressed; reverse influence of the bulk dielectric permittivity is established.

### 743.G1 EFFECT OF ELECTROSTATIC INTERACTIONS ON THE KINETICS OF ADSORPTION OF IONIC SURFACTANT: THEORY AND EXPERIMENT

Ivan U. Vakarelsky, Krassimir D. Danov, Petia M. Vlahovska

Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry,  
University of Sofia, 1 James Bourchier Avenue, Sofia 1126, Bulgaria

A new and exact mathematical solution of the electro-diffusion problem describing the kinetics of ionic surfactant adsorption is obtained. Presence of added symmetric electrolyte is also taken into account. The electro-diffusion of all ionic species in the solution is accounted for. Considering small initial deviation from the equilibrium, the system of non-linear differential equations is linearized and solved applying Laplace transformation. In the absence of added electrolyte the problem allows an exact analytical solution [1]. The short and long time asymptotics are obtained. Simple expression for the dependence of the characteristic relaxation time on the electrolyte and surfactant concentrations is derived. The influence of the surface potential on the kinetics of adsorption is quantitatively demonstrated using the adsorption isotherms of sodium dodecyl sulfate and dodecyl trimethyl ammonium bromide at various interfaces: water/air, water/heptane, water/decane, and water/petroleum ether.

The theory is applicable not only to adsorption at quiescent interfaces, but also at expanding interfaces, like that of the growing bubble in the maximum bubble pressure method. The von Karman approach for the diffusion boundary layer [2] is utilized to reduce the nonlinear electro-diffusion boundary problem to a set of ordinary differential equations, which is solved numerically. The theoretical model is applied to interpret experimental data for several ionic surfactants obtained by the maximum bubble pressure method.

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### 744.G1 EFFECT OF MICELLES ON THE KINETICS OF ADSORPTION FROM SURFACTANT SOLUTIONS AT LARGE DEVIATIONS FROM EQUILIBRIUM

P. M. Vlahovska<sup>1</sup>, K. Danov<sup>1</sup>, G. Broze<sup>2</sup>, A. Mehreteab<sup>3</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics,

Faculty of Chemistry, University of Sofia, James Bourchier Avenue 1, Sofia 1126, Bulgaria

<sup>2</sup>Colgate-Palmolive R&D, Inc., Avenue du Parc Industriel, B-4041 Milmort (Herstal), Belgium

<sup>3</sup>Colgate-Palmolive Technology Center, Piscataway, New Jersey 08854-5596, USA

A theoretical approach to the kinetics of adsorption on the expanding interface of a micellar surfactant solution is proposed. The extension of the adsorption monolayer leads to a transfer of surfactant molecules from the bulk of solution toward the disturbed interface. The micelles simultaneously diffuse and release monomers to compensate the deficiency of surfactant in the subsurface layer. The nonlinear partial differential equations of mass transfer are reduced to ordinary differential equations, which are solved numerically along with the nonlinearized adsorption isotherm as a boundary condition. Being more general, this theoretical approach is consistent also with the special case of small deviations from equilibrium widely used in the kinetics of micellization [1].

The theory is applied to fit the experimental data for dynamic surface tension of micellar solutions of sodium dodecyl sulfate and sodium polyoxyethylene-2 sulfate measured by the maximum bubble pressure method. The expansion of the bubble surface is accounted for by using the experimental dependence of the bubble size on time. The calculated effective rate constant of micelle decay for sodium dodecyl sulfate turns

out to be sensitive to the mechanism of micelle's disintegration. This provides a possibility to determine the rate constants of the fast and slow processes in the relaxation kinetics of micellization by using a relatively simple experimental technique for dynamic surface tension measurement like the maximum bubble pressure method.

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*J. Colloid Interface Sci.* 183 (1996) 223-235.

## 745.G1

### DYNAMICS OF BILAYER MEMBRANES

**Rong Wang**

*Institute of Biophysics, Academia Sinica, Beijing-100101, China*

The dynamic theory of uniaxial liquid crystals (Ericksen-Leslie theory<sup>1,2</sup>) has been adopted to a two-dimensional thin film, on the assumption that the thickness of the film is negligible in comparison with its surfaces. The liquid crystal film is considered to be in a liquid environment of Navier-Stokes fluids and to undergo mass, momentum and energy exchanges with the surroundings. The so-modified theory is applicable for the study of the hydrodynamic behaviors of lipid bilayers as well as biomembranes<sup>3</sup>.

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## 746.G1 SUPER-LONG RANGE INTERACTION BY COLLOIDAL SLOW DYNAMICS

**Shigeo Yoshino**

*Department of Physics, School of Science, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan*

DLVO theory is the standard one for colloidal interaction, which is supported by a lot of experimental data. As well known, the phenomena of colloid are very complicate, it was a marvelous theory. While there are some experimental results not to be explained by DLVO theory. Since DLVO theory is complete one, we should consider what is difference between the theory and experimental results. We could not suppose that there is an error in the process of development of the theory. If there is an unexplainable experimental results, it shows that experimental condition is essential different from the basic assumption of the theory.

The basic assumption of DLVO theory is static model or colloid particles fix on the space-namely DLVO theory is complete for static condition. It is well known that colloid particle moves at any time called Brownian motion. In generally, it is considered that this fact is independent with colloidal interaction.

As in my previous papers, colloidal particles have super-long range attractive and repulsive forces, and moreover there is super-long range interaction between colloid in high salt solvent. These results suggest that the problem does not exist in DLVO theory, but in the theory about electrolyte. For example, ion atmosphere distribute with spherical symmetry around a spherical colloid. This is very reasonable. And this is the essential part of static model.

Generally speaking, "fluctuation" is important for small scale phenomena likely colloid. What kind of fluctuation is essential. I proposed that the relative fluctuation between colloid and ion atmosphere is essential for super-long range interactions. We can easily observed the dynamic fluctuation of colloid through optical microscope. The movement include not only Brownian motion, but also low frequency fluctuation. This fluctuation mode is lower than 100Hz. This slow mode of fluctuation is the origin of super-long range interaction between colloid. These phenomena are not involved in DLVO theory. These are belong in new field or system in colloid. Then we need new theory for the system.

## 747.G2 BUCKLING OF MONOLAYERS AND SPONTANEOUS EMULSIFICATION: STATICS AND DYNAMICS

R. Granek

*Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel*

We examine the possibility of monolayer *buckling* and spontaneous emulsification which are driven by the head-tail asymmetry of the amphiphilic molecules. This asymmetry is modeled in a few ways. For a pure monolayer at the oil-water interface we use the Helfrich *bending free-energy* with non-zero *spontaneous curvature*<sup>1</sup>. We find that below some positive *critical surface tension*, an hexagonal array of "long-fingers" becomes more stable than the flat surface. We study<sup>2</sup> the growth dynamics of these fingers by balancing the viscous energy dissipation with the power generated by the decrease of interfacial freeenergy. The breakup of these fingers into spherical droplets is studied separately<sup>3</sup>. The fingers are shown to develop a Rayleigh-like instability in which they deform into "beads" which can eventually breakup into spherical droplets whose radius we predict. This process is suggested as a mechanism for *spontaneous emulsification*, in which the radius of the spontaneously created droplets is of the order of the spontaneous radius of curvature and is thus close to its final equilibrium value.

In case of a Langmuir monolayer<sup>1</sup>, this "long-finger" structure is not expected to remain stable against multilayer formation, but may be related to the well-known "collapse" phenomena. Considering a *binary mixture* monolayer with non-zero average spontaneous curvature, we find that it can easily buckle to periodic structures following *composition modulations*. Two kinds of buckling structures are found. One involves a very large amplitude, a counterpart of the "long-finger" structure, and is dominated by the average spontaneous curvature. In this case the composition modulation is "slaved" to the preferred shape. The other structure is of much smaller amplitude, and is induced by the *curvature-composition coupling*. When the *molecular tilt* is non-zero, as often is the case in the liquid condensed phase of Langmuir monolayers, the coupling between curvature and tilt can also give rise to a first-order buckling transition.

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## 748.G2 DYNAMICS OF COLLOIDAL AGGREGATION AND LOCAL ORDERING IN TWO DIMENSIONS

Peter H. F. Hansen and Lennart Bergström

*Institute for Surface Chemistry, YKI, Stockholm, Sweden*

The current knowledge about the mechanisms and the dynamics of colloidal aggregate formation origin mostly from computer simulations. Computer simulations are models and have to be verified by experimental investigations. Experimental studies in two dimensions have proven to be useful for this purpose, as the growth of the clusters can be directly observed by light microscopy and the results directly compared with computer simulations.

During the last decade, there have been several experimental attempts to investigate the two-dimensional aggregation process. However, since most experimental systems have been characterized by ill defined interactions, the interpretation of the aggregation results have been complicated [1,2].

In this presentation, we will present a novel two-dimensional colloidal system with well defined interactions. The system consists of hydrophobic silica particles partly immersed in an organic liquid, giving a good control of the particle interaction. The interaction forces can be modulated by using surfactant coatings of different chain lengths and different organic liquids. This kind of system has previously been used to produce a porous monolayer of silica particles [3].

The aggregation dynamics have been continuously studied by an optical microscope. The structures have been registered through a CCD camera and analysed by an image processing system. The dynamics of the cluster-cluster aggregation will be discussed by means of fractal dimensions and pair-distribution functions for different particle interactions.

Our aim is to obtain a deeper understanding of the relation between the particle-particle interactions and the global structure of a colloidal monolayer. We believe that the existence of such relations in other systems, e.g. in the condensation of simple liquids and quasi crystals, may provide some further insight. At a later stage, the experimental results will be compared with computer simulations.

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## 749.G2

### MOLECULAR ADSORPTION VS. CELL ADHESION AT THE DROPPING MERCURY ELECTRODE

Solveg Kovac, Vera Zutic and Vesna Svetlicic

Center for Marine Research, Rudjer Boskovic Institute, Zagreb, Croatia

Studies of biofilm formation are essential for understanding and control of processes in natural aquatic systems, for industrial applications and in medicine and stomatology where the most extensive studies have been performed (1). Our investigations of adhesion of droplets (2) and microorganisms (3,4) at the expanding mercury electrode/seawater interface offer a new approach to studies of initial monolayer formation in complex mixtures of dissolved and dispersed surfactants.

Dynamics of film formation is measured as a time which is necessary to reach a full coverage at the fast dropping mercury electrode in the scale 10-2000 ms by adsorption of dissolved biomolecules and/or adhesion of cells suspended in an aqueous electrolyte solution. Phytoplankton organism *Dunaliella tertiolecta* (8-10µm) has been chosen as a model organism. It has fluid cell wall and the attachment of individual cells at the mercury electrode yields well-defined electrical signals in millisecond scale, and amplitudes 0.6-2.2 µA. Measurable concentration range  $10^3$ - $10^5$  cells/ml was limited by frequency of attachment signals (0.05-10 signals per 2 seconds). Dextran, albumine and nonionic detergent Triton T-X-100 were chosen as soluble molecules in concentration range 0.05-500 mg/l. Measurement of attachment signals of *Dunaliella tertiolecta* cells is proposed to probe mechanisms of transport and adsorption process in the molecular film formation.

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4. V. Svetlicic, N. Ivosevic, V. Zutic, Croat.Chem. Acta, in press.

## 750.G2

### PHOSPHOLIPID-MONOLAYERS - ORDER OF PHASE TRANSITION AND DYNAMIC PROPERTIES

G. Kretzschmar<sup>1</sup>, J.B. Li<sup>2</sup>, R. Miller<sup>1</sup>, H. Möhwald<sup>1</sup>, A.W. Neumann<sup>3</sup>

<sup>1</sup>Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Berlin, F.R.G.

<sup>2</sup>Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, China,

<sup>3</sup>Dept Mech. Engineering, University Toronto, 5 King's College Road, Toronto, M5S 1A4 Canada

The determination of the order of phase transition from liquid-expanded to liquid condensed surface phases is strongly influenced by the experimental conditions. For example, special care has to be taken with respect to the temperature control of an extended monolayer. Other significant influences on the shape of the monolayer isotherm are the kind of spreading solvent, the conditions of spreading and the time scale of the complete procedure. This allows to understand the discrepancies between statements made in the literature by different authors on the order of phase transition of this sensitive system. By choosing special experimental conditions a first-order phase transition in spread phospholipid monolayers is evident.

When harmonic area change is applied to a monolayer a harmonic surface pressure change results showing a loss angle to the wave generation. From the surface pressure amplitude and the phase shift the

dilational elasticity and viscosity can be deduced. DPPC and DMPE monolayers exhibit a minimum in the elasticity and viscosity within the transition region.

The harmonic compression and dilatation of the monolayer induces two main relaxations. At first there is a propagation of longitudinal surface waves and their damping. The velocity of longitudinal (elastic) waves are strongly influenced by the elasticity of the monolayer. Second there is a formation of a surface pressure gradient leading to a Marangoni flow. Both processes are part of the monolayer relaxation and contribute to the loss angle. Wave vector, Marangoni effect and the velocity of the elastic waves, respectively, generated by an oscillating barrier lead to a superposition of the area occupied by molecules at the interface.

Systematic experiments and a Fourier analysis of the results allow to get new information on dynamic monolayer properties. For example pronounced shifts in the Fourier coefficients are detected in the frequency range of barrier oscillation from 0.18 Hz to 0.05 Hz. In general one can conclude that dissipative processes play the dominant role in the dynamic behaviour of spread monolayers of phospholipids. The effects controlling this dynamic system can be described by the mechanism of domain formation/dissolution in the monolayer. In a recent paper Kretzschmar, Li, Motschmann, Miller and Möhwald (Colloids & Surfaces A, 114(1996)277) have given some evidences for the influence of the domain structures on the dynamic monolayers properties of DPPC and DMPC.

## 751.G2

### VISCOELASTICITY OF PHOSPHOLIPID LAYERS AT DIFFERENT FLUID INTERFACES

J. B. Li<sup>1,2</sup>, G. Kretzschmar<sup>2</sup>, M. Bree<sup>2</sup>, R. Miller<sup>2</sup> and H. Möhwald<sup>2</sup>

<sup>1</sup>International Joint Lab between Institute of Photographic Chemistry and Max Planck Institute  
of Colloids and Interfaces, De Wai, Bei Sha Tan, 100101, Beijing, China

<sup>2</sup>Max Planck Inst. of Colloids and Interfaces, Rudower Chaussee 5, D-12489, Berlin-Adlershof, Germany

The interfacial relaxation behaviour of phospholipids, L- $\alpha$ -dipalmitoyl phosphatidylcholine (DPPC) and L- $\alpha$ -dimyristoyl phosphatidylethanolamine (DMPE), as soluble adsorption layers at the water/chloroform interface and as insoluble spread monolayers at the air/water interface have been investigated.

Transient area changes of the pendent drop by definite increments after a quasi-equilibrium status studied by axisymmetric drop shape analysis (ADSA) produce an interfacial relaxation response of the phospholipids adsorption layers at the liquid/liquid interface. Dynamic interfacial tension response to square pulse area disturbances of surface equilibrium was measured in the time domain. From this response functions information on the exchange of surfactants and the interfacial dilational elasticity of phospholipids has been obtained.

A modified Langmuir trough with an oscillating barrier was used to investigate the relaxation behaviour of insoluble spread monolayer. The harmonic area perturbation generated by a barrier initiates relaxation processes in the monolayer. The surface pressure amplitude and phase shift yield the dilational elasticity and viscosity of DPPC and DMPE monolayers. Effect of oscillating frequency on the viscoelasticity of phospholipids monolayer has been explored as well.

Possible origins of the relaxation for soluble and insoluble phospholipid layers at different fluid interfaces are discussed.

## 752.G2

### SURFACE WAVE SCATTERING BY TWO-DIMENSIONAL COLLOID SYSTEMS

B. A. Noskov

Chemical Faculty, St.Petersburg State University, St.Petersburg, Russia

Insoluble surface films at the air-water interface have been investigated by the capillary wave method for many years. However, it is only recently that the possibility to extract some characteristics of their macroscopic structure by this technique has been realized<sup>1</sup>. For example, the heterogeneity of monolayers of fatty acids at low surface pressure influences the dependency of the damping coefficient on the area per molecule and this effect depends on the spreading conditions and the nature of the surfactant<sup>2</sup>. At the same time, further progress in this field is restrained for the lack of an elaborate theory. The main aim of

this work is to present results of the theoretical study of surface wave propagation along the liquid surface covered by a heterogeneous insoluble film. Some results related to the wave diffraction on a single two-dimensional circular particle have been published earlier<sup>3,4</sup>. An approximate solution of the corresponding boundary problem for the hydrodynamic equations leads to a relation for the scattering amplitude. This work deals with a more general situation. Surface waves go through and are scattered by a concentrated two-dimensional colloid system. The behaviour of the scattering medium is described with the use of the effective complex propagation constant taking into account multiple scattering effects. An equation for the effective wave number is derived which allows us to calculate this quantity on the base of the scattering amplitude and the surface coverage. The effects of multiple scattering are negligible for equilibrium fluid films containing "islands" of condensed surface phases. However, for non-equilibrium systems with heterogeneous continuous solidlike surface phase the dependency of the real part of the effective wave number on the concentration of scatterers can be non-linear. Inhomogeneity of the dynamic surface elasticity influences the effective characteristics of transverse waves only in the case of a continuous condensed film with two-dimensional "bubbles" of gaseous phase. The last situation was probably realized in the course of recent experimental studies of the transitional region between gaseous and liquid-expanded two-dimensional phases by the capillary wave method.

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## 753.G2

### DEWETTING, PARTIAL WETTING AND SPREADING OF A MONOLAYER ON SOLID SURFACE

G. Oshanin<sup>1</sup>, J. De Coninck<sup>1</sup>, A.M. Cazabat<sup>2</sup>, M. Moreau<sup>3</sup>

<sup>1</sup>*Université de Mons-Hainaut, Centre de Recherche en Modélisation Moléculaire,  
20 Place du Parc, 7000 Mons, Belgium*

<sup>2</sup>*Laboratoire de Physique de la Matière Condensée, Collège de France,  
11 Place M. Berthelot, 75231 Paris Cedex 05, France*

<sup>3</sup>*Laboratoire de Physique Théorique des Liquides, Université Paris VI,  
4 Place Jussieu, 75252 Paris Cedex 05, France*

We study behavior of a monolayer, which occupies initially a macroscopically large bounded region on an ideal crystalline surface and then is let to evolve in time due to random hopping motion of the monolayer particles. Monolayer in such a non-equilibrium configuration appears, for instance, at the late stages of droplet spreading, when the drop feeding the precursor film runs out, or in the situation, in which a homogeneous monolayer is perturbed by nucleation of a dewetted region. Other possible applications include uptake of liquids in nanopores, the Ostwald ripening of voids or island formation in 2D adlayers. In case when the initially occupied region is the half-plane  $X < 0$  we determine explicitly, in terms of an analytically solvable mean-field-type approximation, the time evolution of the mean displacement  $X(t)$  of the monolayer edge. We find that at sufficiently large times  $X(t)$  obeys  $X(t) = A(D_0 t)^{1/2}$  where  $t$  is time,  $D_0$  is the diffusion coefficient and the prefactor  $A$  is a function of the temperature and the particle-particle interactions. We show that depending on the physical conditions  $A$  can be greater, equal or less than zero and specify the critical parameter which distinguishes between the regimes of spreading ( $A > 0$ ), partial wetting ( $A = 0$ ) and dewetting ( $A < 0$ ). Our theoretical predictions agree with the experimental results on spreading of molecularly thin films.

## 754.G2

### THERMODYNAMIC STUDIES OF NATURAL MARINE SURFACE FILMS IN THE BALTIC SEA

Stanislaw.J. Pogorzelski

*Institute of Experimental Physics, University of Gdansk, Gdansk, Poland*

Natural surface film experiments in shallow offshore waters of the Baltic Sea were carried out using a novel device for sampling and force-area studies [Pogorzelski, 1992, *Rev. Sci. Instrum.* 63, 3773-3776].

The integrated sampler- Langmuir trough trough "cuts out" an indisturbed film-covered sea area to be studied "in situ" and water samples are untreated chemically. The compression-expansion isotherms were collected in six stations along the South Baltic shore line in Poland at different temperatures (from the range 10-40 Celsius degrees). The apparent isotherm hysteresis allowed the isotherm reversibility (related to the entropy change), film elasticity, density of deformation energy converted to heat in the process obeying a Carnot cycle to be determined. They turned out to be different for the samples collected at the surface and these diffusionally formed from the 0.5 m.-deep subsurface water at the same measuring field. The isotherms, determined using Langmuir trough-Wilhelmy filter paper plate technique exhibited several phase transitions evidently not of the first order, the transitions of both thermodynamic and kinematic type were observed. Isotherms taken at different temperatures  $T$  were used to create phase diagrams  $p$ - $T$  (significantly different in reference to the fatty acid ones, for instance), and then to compute the 2D phase transition border lines, finally leading, by applying Classius -Clapeyron equation, to the phase transition heat. It has been shown that the elastic film parameters are subjected to large seasonal and spatial variability [Pogorzelski et.al., 1994, Cont. Shelf Res. 14, 1621-1643], moreover the complex structure of natural films depends on environmental factors (surfactant concentration, pH, ionic strength of the subphase,  $T$ , and others). [Pogorzelski, 1996, Colloids and Surfaces, A, 114, 297-309]. Similarly, the selected thermodynamic quantities are correlated to environmental factors as well.

## **755.G2 DYNAMICS OF FILM FORMATION AT THE EXPANDING MERCURY SPHERE IN CONTACT WITH CELL SUSPENSION**

**Vesna Svetlicic<sup>1</sup>, Igor Zutic<sup>2</sup>**

<sup>1</sup>*Center for Marine Research, Rugjer Boskovic Institute, Zagreb, POB 1016, 10001 Croatia,*

<sup>2</sup>*Department of Physics and Astronomy, University of Minnesota, Minneapolis, MN 55455, USA*

Surface growth rate of the dropping mercury electrode can be used to evaluate dynamics of film formation at an aqueous suspension/mercury electrode biterface. A fast dropping mercury electrode, among other attributes such as hydrophobicity and controlled surface charge, mimics interfacial dynamics of natural fluid interfaces: interfacial tension gradients and increased transport from suspension by convective streaming and turbulence in adjacent layers. Film formation at the dropping mercury electrode immersed in an aqueous solution of microorganisms involves the following steps: transport and attachment of cells, spreading of attached cells at the interface and coalescence of spreading zones to form a film. Transport control can be eliminated in dense cell suspensions, while attachment and spreading rates can be maximised through adjusting interfacial tension by selection of the electrode potential. Coalescence of spreading zones of individual cells thus becomes the rate limiting step and for most of microbial films studied has a subsecond time range. A model was developed based on experimental results obtained in algal (diameter 10 $\mu$ m) and bacterial (0.5 to 3 $\mu$ m length) cell suspensions. Surface area of the expanding mercury sphere varied nonlinearly from 0 to 4.7 mm<sup>2</sup> within 2 seconds and the maximum surface area of spreading zones of a single cell was 2x10<sup>2</sup>  $\mu$ m<sup>2</sup> (bacterial cell) and 10<sup>4</sup>  $\mu$ m<sup>2</sup> (algal cell).

## **756.G2 STRUCTURE AND HYDRATION OF SUPPORTED LIPID MONOLAYERS FROM POLARIZED ATTENUATED TOTAL REFLECTION INFRARED SPECTROSCOPY**

**Suren A. Tatulian**

*Dept. of Molecular Physiology and Biological Physics, Univ. of Virginia Health Sciences Center,  
P.O. Box 10011, Charlottesville, VA 22906-0011, USA.*

Lipid monolayers were deposited onto a germanium internal reflection plate by Langmuir-Blodgett technique and the lipid surface concentration, phase state, orientational order, hydration and monolayer-Ge separation were determined by polarized attenuated total reflection (ATR) infrared (IR) spectroscopy. A diacylglycerol: dipalmitoylglycerol (DPG), a dialkyl-phosphatidylcholine: dihexadecyl-phosphatidylcholine (DHPC), and three diacyl-phosphatidylcholines: dipalmitoyl-, dimyristoyl-, and 1-palmitoyl-2-oleoyl-phosphatidylcholine (DPPC, DMPC, and POPC) were used to study the effect of the lipid hydrocarbon chain and



the headgroup on the structure and hydration of lipids in monolayers. An ATR IR spectrum of a supported POPC monolayer is shown in Figure 1.

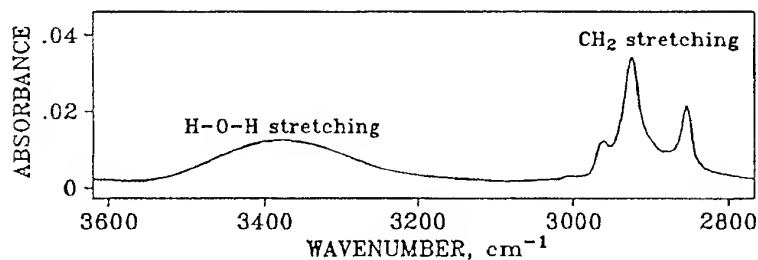


Figure 1. An ATR IR spectrum of a POPC monolayer deposited on a germanium internal reflection plate in the region of water H-O-H and lipid CH<sub>2</sub> stretching vibrations at parallel polarization of the IR light.

Integrated absorbencies due to lipid CH<sub>2</sub> stretching vibrations were used to estimate the lipid surface concentrations. Both the area per lipid molecule and  $\nu(\text{CH}_2)$  increased in the sequence: DPG<DHPC<DPPC<DMPC<POPC, indicating an increase in motional freedom of the lipids and decrease in the packing density with increasing headgroup dimensions and hydrocarbon chain unsaturation and decreasing chain length. The presence of ester carbonyl groups decreased the lipid packing density from 0.022 Å<sup>-2</sup> (DHPC) to 0.017 Å<sup>-2</sup> (DPPC). The lipid orientational order parameters were  $S_L = 0.71$ -0.56, indicating average tilt angles of 26-33° for the lipid hydrocarbon chains. The H<sub>2</sub>O/Lipid molar ratios were estimated as  $A(\text{H}_2\text{O}) \cdot \epsilon_{\text{Lipid}} / A(\text{Lipid}) \cdot \epsilon_{\text{Water}}$ , where  $\epsilon$  is the corresponding molar absorption coefficient, and were used to find the monolayer-substrate separations. The number of waters per lipid increased from ~2 to ~10 according to the above sequence, and the monolayer-substrate separation was 2-4 Å, indicating a single layer of trapped water molecules between the lipid monolayer and the germanium substrate. The results are summarized in the Table below.

Lipid	$A_{\text{H}}(\text{Lipid})$	Å <sup>2</sup> /lipid	$R_L^{\text{ATR}}$	$S_L$	$\nu_{\text{as}}(\text{CH}_2), \text{cm}^{-1}$	$A_{\text{H}}(\text{H}_2\text{O})$	H <sub>2</sub> O/L	h, Å
DPG	4.87	35.7	1.11	0.63	2916.5	0.92	2.1	1.8
DHPC	4.13	44.8	1.08	0.67	2917.1	1.93	5.4	3.6
DPPC	2.98	58.4	1.06	0.71	2917.8	1.80	6.6	3.4
DMPC	2.19	69.0	1.09	0.66	2921.7	1.97	8.6	3.7
POPC	1.96	91.7	1.17	0.56	2922.8	1.64	9.4	3.1

$A_{\text{H}}(\text{Lipid})$  is the absorbance due to lipid hydrocarbon chain CH<sub>2</sub> stretching vibrations at parallel polarization of IR light, integrated between 2980 and 2820 cm<sup>-1</sup>;  $R_L^{\text{ATR}}$  and  $S_L$  are the lipid ATR dichroic ratio and the orientational order parameter, respectively;  $\nu_{\text{as}}(\text{CH}_2)$  is the wavenumber of the asymmetric CH<sub>2</sub> stretching vibration;  $A_{\text{H}}(\text{H}_2\text{O})$  is the absorbance due to H-O-H stretching vibration of the trapped water at parallel polarization of IR light, integrated between 3540 and 3230 cm<sup>-1</sup>; H<sub>2</sub>O/L is the water/lipid molar ratio; h is the monolayer-substrate separation.

## 757.G2

### KINETICS OF RELAXATION AND DISSOLUTION OF MIXED MONOLAYERS OF CATIONIC AND ANIONIC AMPHIPHILES

Maria Isabel Viseu, Amélia M. Gonçalves da Silva, Sílvia M.B. Costa  
Centro de Química Estrutural, Instituto Superior Técnico, Lisboa, Portugal

Aqueous solutions of mixtures of oppositely-charged ionic surfactants present usually high synergism in their solution and interface properties, due to the strong attractive interactions between their components<sup>1</sup>.

Synergistic effects are also invoked in the present work to explain the formation of condensed monolayers from equimolar mixtures of cationic and anionic amphiphiles at the air-water interface at 298 K. In fact, among the pure surfactants used, only the double-chained 2C<sub>18</sub>A<sup>+</sup> and 2C<sub>12</sub>A<sup>+</sup> (where A<sup>+</sup> stands for the dimethylammonium ion) form fluid monolayers, whereas the single-chained C<sub>n</sub>A<sup>+</sup> and C<sub>n</sub>S<sup>-</sup> (where A<sup>+</sup> now represents trimethylammonium, S<sup>-</sup> stands for sulfate, and n = 16, 14, or 12) are readily soluble in the water subphase. The kinetics of relaxation and the stability of the monolayers of five selected systems obtained from equimolar cationic-anionic combinations of the above amphiphiles were studied. The surface pressure-time ( $\pi$ -t) isotherms were recorded at constant surface area, after compression of the spread monolayer up to an adequate target pressure. The decay curves obtained show two main regimes: at shorter times, up to ca. 10-15

minutes, a fast relaxation process dominates the decay, decreasing the pressure up to a final, equilibrium value; at longer times, a second process is also evident, which slowly decreases the pressure below the equilibrium value attained by relaxation.

The decay curves could be reasonably fitted to a sum of 3 exponentials, two of them with lifetimes of the order of a few minutes and the third one with a lifetime of several hundreds of minutes. The two faster processes, whose magnitude depended on the speed at which the film had been previously compressed and on the target pressure, were attributed to a complex reorganization mechanism of the charged head-groups and tails in the monolayer after the sudden stopping of the compression. The third, longer lifetime process, which depended on the compression target pressure, was attributed to a slow dissolution of the film into the subphase. The results are discussed in terms of a possible kinetic scheme involving both reorganization and dissolution mechanisms, and are compared for the five systems studied.

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## 758.G3

### RHEOLOGICAL PROPERTIES OF LUPIN (LUPINUS ALBUS ssp. GRAECUS) PROTEINIS OLATE FILMS AT THE CORN OIL-WATER INTERFACE

S. Alamanou and G. Doxastakis

Laboratory of Food Chemistry and Technology, Faculty of Chemistry,  
Aristotle University of Thessaloniki, 54 006 Greece

This poster presents the results of research conducted over the last year in the Laboratory of Food Chemistry and Technology of the University of Thessaloniki on the rheological properties of Lupin seed protein isolate films at the corn oil-water interface obtained by methods such as isoelectric precipitation and dialysis from full fat or defatted flour with or without NaCl. The methods varied in their effectiveness in removing soluble proteins fractions, polysaccharides, toxic quinolizidine alkaloids and other components which highly alter the rheological properties of their products.

## 759.G3

### INTERFACIAL RHEOLOGICAL PROPERTIES MEASURED BY THE EXPANDING DROP METHOD AND THE EXTENDED MAXIMUM BUBBLE PRESSURE METHOD

L. N. Arnaudov<sup>1</sup>, G. S. Marinov<sup>1</sup>, G. Broze<sup>2</sup>, and A. Mehreteab<sup>3</sup>

<sup>1</sup>Laboratory of Thermodynamics and Physico-chemical Hydrodynamics, University of Sofia,  
Faculty of Chemistry, 1, James Bourchier Avenue, 1126 Sofia, Bulgaria,

<sup>2</sup>Colgate-Palmolive Research and Development, Inc., Avenue Du Parc Industriel,  
B-4041 Milmort (Herstal) Belgium,

<sup>3</sup>Colgate-Palmolive Company, Technology Center, 909 River Road, Piscataway, New Jersey 08854-5596

The aim of the study is to develop a new method for obtaining surface rheological parameters, which are more important than the dynamic surface tension from a practical view point, from the extension of the known maximum bubble pressure method (MBPM). The applied experimental technique is a modification of the experiment performed by MBPM involving a video record of the bubble image during its growth and detachment. We propose a new theoretical model for diffusion controlled adsorption at small deviations from *non-equilibrium initial state*. This model makes possible the interpretation of experimental data from the MBPM even though the initial condition for the diffusion problem is not the equilibrium one. We performed rheological experiments with non-ionic surfactant by using the new experimental technique and compared the results to the already known expanding drop method. By fitting the experimental data we obtained the surface elasticity of the surfactant adsorption layer as a function of the subsurface surfactant concentration and compared the results from the two techniques. The new theoretical model gives an excellent fit of the experimental data. We also calculated the Gibbs elasticity by using the surface tension isotherm and compared it to the experimental results. The obtained results are encouraging and show that the MBPM can be used as a rheological tool.

## 760.G3 SURFACE AND PARTICLE STRUCTURES OF HYDROPHILIC AND SilyLATED FUMED SILICA

H. Barthel, M. Heinemann, L. Rösch and J. Weis

Wacker-Chemie GmbH, Werk Burghausen, D-84480 Burghausen, Germany

Fumed silica is an amorphous silicon dioxide produced from a pyrogenic process by burning silicon tetrachloride in an oxygen-hydrogen flame. Fumed silica finds wide use in a variety of industries. Main applications are the control of the rheological properties of liquids, the active reinforcement of elastomers and the improvement of the flowability of powders. The technical performance of this highly dispersed silica is strongly related to adsorption interactions at the surface and to the very peculiar spacial structure of fumed silica particles. The aim of this paper is to relate the surface and particle structures of the product to the particular steps of the production process. Freshly produced fumed silica appears to be a fluffy white powder of an extremely low bulk density in the range of about 20 g/l, although the density of amorphous silica itself is of about 2200 g/l. The concept of fractal dimensions turns out to be a helpful tool in order to study fumed silica surface and particle structures [1]. In the flame, silicon dioxide protoparticles are formed during the high temperature hydrolysis of the chlorosilane [2]. Contact and fusion lead to so-called primary particles, exhibiting smooth surfaces. Collision and partial fusion of these primary particles in the flame result in stable silica aggregates, isolated primary particles are not existing in fumed silica. The structure of these aggregates is described by a diffusion limited aggregation (DLA) of particles. Leaving the flame and cooling down, agglomerates of aggregates are built up, hold together by physico-chemical surface interactions. The formation of these agglomerates follows a reaction limited cluster-cluster agglomeration (RLCA). Surface silylation using trimethylsiloxy or dimethylsiloxy groups grafted on silica silanols are useful tools to control the silica surface energy. In this study, a model is presented to describe the particle structures of fumed silica, and the size distributions, as a dynamic system. Depending on the analytical methods used, different ranges of particles size distributions have to be considered. Data from laser light scattering and laser light diffraction of silica in different media are compared to those from electron microscopy. Small angle X-ray scattering and static volumetric gas adsorption of nitrogen and argon have been used to investigate both surface and mass fractal dimensions of different grades of bare and silylated fumed silica. The rheological behavior at different shear rates of liquids thickened by fumed silica are discussed in terms of surface interactions together with surface fractal dimensions and the mass fractal dimension of silica aggregates and agglomerates.

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## 761.G3 INHOMOGENEOUS SHEAR FLOW OF WORMLIKE MICELLES

Jean-François Berret<sup>1</sup>, Grégoire Porte<sup>1</sup>, James L. Harden<sup>1</sup>, J.-P. Decruppe<sup>2</sup>

<sup>1</sup>Groupe de Dynamique des Phases Condensées, cc026, Unité Mixte de Recherche N°5581

C.N.R.S./Université de Montpellier II, F-34095 Montpellier cedex 05 France,

<sup>2</sup>Laboratoire de Physique des Liquides et Interfaces, Groupe de Physique des Colloïdes et Polymères, Université de Metz, 57078 Metz - France

Combining nonlinear rheology, flow birefringence (FB) and small-angle neutron scattering (SANS) under shear, we have investigated semidilute solutions of wormlike micelles made of surfactant molecules. From their linear mechanical responses, these complex fluids are identified as pure Maxwellian fluids, i.e. the stress relaxation function reads  $G(t) = G_0 \exp(-t/t_R)$ , where  $G_0$  is the elastic modulus and  $t_R$  the relaxation time describing the dynamics of the wormlike chains. When subjected to steady shear, however, wormlike micelles are found to undergo a transition toward an inhomogeneous state of flow. This transition manifests itself through a plateau in the shear stress *versus* shear rate behavior. In the plateau regime, flow birefringence measurements in the direction of the vorticity (in standard Couette flow) enables a direct visualisation of the two coexisting phases. One is strongly birefringent, the other remains isotropic. Since the oriented birefringent phase is much more fluid than the isotropic one, it supports a larger velocity gradient : the flow is thus strongly inhomogeneous [1]. We propose a phenomenological explanation of these results in

terms of an effective nonequilibrium potential that accounts for the free energy stored in a viscoelastic material under steady shear conditions [2]. This model relies on at least two observations which present striking analogies with ordinary field-induced phase transitions in equilibrium systems, namely: the robustness of the two-state banded-flow regime and the kinetics of the band formation under shear. Investigated using transient rheological measurements, this kinetics has revealed regimes of nucleation-and-growth (in the domain of metastability) as well as of spinodal decomposition [3]. Within this picture, a shear-thinning non-homogeneous flow can be shown to be a manifestation of some underlying structural transition.

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2. G. Porte, J.-F. Berret et J.L. Harden, Non Homogeneous Flows of Complex Fluids: Mechanical Instability Versus True Phase Transition, *Journal de Physique II* 7, 1 -6 (1996).
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## 762.G3 INTERFACIAL RHEOLOGY. INTERFACIAL DIFFUSIVITY AND SHEAR AND DILATATIONAL INTERFACIAL VISCOSITY

**Krassimir D. Danov, Ivan B. Ivanov, Jordan T. Petkov, Liuben N. Arnaudov**

*Laboratory of Thermodynamics and Physico-Chemical Hydrodynamics, Faculty of Chemistry,  
University of Sofia, James Bourchier Avenue 1, Sofia 1126, Bulgaria*

New constitutive equations for the surface diffusion and heat fluxes, shear and dilatational viscosities are obtained using the Onsager theory for the surface-excess dissipation function. For that purpose the non-equilibrium thermodynamics of a mixture of surfactants in the presence of chemical reactions between them is developed. It is proved that the interfacial shear stress depends only on the surface shear strain. In contrast, the dilatational part of the constitutive relation contains contributions of the surfactant diffusion, interfacial chemical reactions and the adsorption of counter-ions from the bulk-phases. The dilatational viscous stress is proportional to the relative increase of the area per molecule instead to the relative change of the total area as commonly adopted in the literature.

Experiments with solution of high-molecular mass surfactants consisting of surface expansion and stress relaxation measurement are carried out. Precise computer control of the system is ensured. The data are interpreted by means of the proposed rheological equations and results for the Gibbs elasticity and interfacial dilatational viscosity are obtained.

A new method for determination of the shear viscosity of low-molecular surfactant monolayers is described. The method is based on the measurement of the drag coefficient of a millimeter sized sphere, attached to the interface [1]. The theoretical predictions, based on the numerical solution of the Stokes equation with two-dimensional Boussinesq-Scriven interfacial rheology law, are tested against experimental data. Brownian motion of a particle is taken into account and the numerical results reveal for all contact angles a strong decrease of the surface diffusion coefficient when the surface viscosity increases [2].

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## 763.G3 A SURFACE CHEMISTRY STUDY ON REDUCING VISCOSITY OF CONCENTRATED KAOLIN SUSPENSIONS

**Gong Wenqi, Bao Jianlong, Wu Xiaohuan**

*Department of Resources and Environmental Engineering, Wuhan University of Technology,  
Wuhan, P. R. China*

Factors affecting the viscosity of the concentrated suspensions of suzhou kaolins were studied. Experiments were carried out to use different kinds of dispersants to reduce the viscosity of the concentrated kaolin suspensions. The results indicated that good effects of reducing the viscosity of the kaolin suspensions were obtained by using the combination of dispersants D I and D III, or D III and IV, respectively. The viscosity of the kaolin suspensions was reduced from greater than 10,000 mPa·s to less than 500 mPa·s.

Analytical tests indicated that the surface properties were the major factors affecting the viscosity. The effect of dispersants was to change the surface properties rather than the structure of the minerals in the kaolin ores. The addition of the dispersants increased the hydrophilicity of particle surfaces and the electrostatic repulsion between particles, resulting in improved dispersion and flow ability of the concentrated kaolin suspensions.

## 764.G4 STRUCTURAL EFFECTS AND RHEOLOGY OF PEO-PPO-PEO TRIBLOCK COPOLYMER SOLUTIONS

Ya. Ivanov<sup>1</sup>, R.Kotsilkova<sup>1</sup>, E. Krusteva<sup>1</sup>, N. Antonova<sup>2</sup>

<sup>1</sup>Central Laboratory of Physico-Chemical Mechanics, Acad.G. Bonchev Str., Bl. 1, 1113 Sofia, Bulgaria

<sup>2</sup>Laboratory of Biodynamics and Biorheology, Institute of Mechanics and Biomechanics, Bulgarian Academy of Sciences, Acad. G.Bonchev Str., Bl 4, 1113 Sofia, Bulgaria

The relationship between the structure formation and the rheological properties of aqueous PEO-PPO-PEO triblock copolymer solutions has been investigated. The changes in the rheological behaviour and properties and their dependence on polymer concentration, on the amount of the added electrolytes and on the shear rate gradient are demonstrated. The critical concentrations when the  $\tau_{\max}/\tau_{st}$  ratio passes through a maximum ( $\cong 1$ ) have been determined. The influence of the electrolyte admixture is studied on the viscosity and on the thixotropic effects for different concentrations of the polymer is studied. The observed structural effects are described with the equation of Martin and they are related to the processes of micelle formation. It has been established that the strength of the formed structure is considerably increased with micelle growth, initiated by the increased electrolyte concentration.

An attempt is made to model the changes in the viscosity of the systems due to the variation of polymer concentration in the presence or absence of electrolytes.

The present investigations have been performed with the partial financial support of the National Fund "Scientific Investigations" (project No X-311).

## 765.G3 ON THE RHEOLOGY AND THINNING OF FOAM FILMS FROM AQUEOUS SOLUTIONS OF AN ABA TRIBLOCK COPOLYMER

Ya. Ivanov<sup>1</sup>, R. Kotsilkova<sup>1</sup>, R. Sedev<sup>2</sup>, T. Kolarov<sup>2</sup>, E. Krusteva<sup>1</sup>, and D. Exerowa<sup>2</sup>

<sup>1</sup>Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

<sup>2</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

The thinning of foam films obtained from aqueous solutions of an ABA triblock copolymer of polyethylene oxide and polypropylene oxide (Synperonic PE F108,  $M = 14000$ ) is studied. The influence of copolymer concentration, electrolyte concentration and shear rate on the rheological behavior and properties is investigated. The parameters obtained by physico-chemical and rheological methods are compared. A tentative interpretation of the relation between rheological behavior and properties and film thinning is given. On this basis some implications concerning the practical application of the solutions of such copolymers are discussed.

## 766.G3 RHEOLOGICAL PROPERTIES OF PROTEIN LAYERS AT LIQUID INTERFACES

V.N. Izmailova

Department of Colloid Chemistry, Moscow State University, Vorob'evy Gory, Moscow 119899, Russia

Proteins are natural surface active substances. Surface phenomena are far and wide spread both in nature and technology. Investigations of protein interface layers (PIL) are of importance for the development of conceptions of emulsion and microemulsions stability, when protein are used as stabilizers.

Structure-rheological properties of PIL are the most sensitive characteristics to any changes of the system, because of this rheological measurements on the level with other available methods were performed for a number of systems. Surface activity of protein is connected with spatial structure of its molecule as well as surface topography, providing a asymmetrical location polar and nonpolar atom groups on the protein surface. To evaluate changes of the conformation of protein adsorbed at interfaces, methods of dispersion of optical rotation, CD, MNR relaxation and catalytic properties of enzymes determinations were used in our works.

To control rheological properties of PIL a forced protein complex formation in aqueous solution with different substances (dextran sulfate, lipids as well as low molecular mass surfactants) were wide used. In many cases the production of complexes is resulted in enhancing of the surface activity. This was recorded by means of measurements of interfacial tension isotherms. In the process of protein accumulation at an interface there is a probability of two-dimension phase transition with the formation of interfacial structures of the coagulation, condensation-crystallization nature, as well as ordered ones due to long range interactions of elements of the structure. Conditions were determined, when PIL, according to its rheological parameters, behaves as solid-like body, revealing module of elasticity, critical shearing stress, viscosity and time of relaxation. Hydrocarbon solubilization, as it has been established, affects on the equilibrium achievement in systems of protein aqueous solution coupled with oil phase. Side by side with PIL formation a partitioning of protein in a composition of associated particles between two liquid phases is observed resulting in the transition of the system to a steady state. These results were obtained using method of radioactive indicator with tritium labeled proteins. The correlation is determined between PIL properties and formation of black foam and emulsion films, considered as models of stable foams and emulsions.

### 767.G3 PSEUDOPLASTICITY OF FILTRATION CAKES EXPLAINS CROSS-FLOW MICROFILTRATION BEHAVIOUR

E.D. Krusteva<sup>1</sup>, T.A. Doneva<sup>2</sup>, C.S. Vassilieff<sup>2</sup>

<sup>1</sup>Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Science, 1113, Bulgaria,

<sup>2</sup>Laboratory of Biophysical Chemistry, Department of Physical Chemistry,  
University of Sofia, 1126, Bulgaria

The rheological behaviour of polydisperse bentonite and monodisperse latex suspensions is established experimentally. Both exhibit a pronounced pseudoplasticity which diminishes with diminishing particulate concentration. The rheological data are parameterized making use of different empirical rheological "models".

During continuous microfiltration in cross-flow mode the filter cake is subject to tangential stress. Depending on rheological properties and hydrodynamic condition the cake may be tangentially mobile or immobile. According to the convective model of microfiltration tangential outflow of a mobile cake can ensure continuous operation.

Taking into account the contribution of diffusive back transport the approximate analytical expression of the convective model and cross-flow microfiltration experimental data are used to estimate indirectly the non-Newtonian ("apparent") viscosity of the concentrated filtration cakes. These indirect estimates are in reasonable agreement with the direct rheological results.

### 768.G3 EFFECT OF INORGANIC ELECTROLYTES AND ALKALINE MATERIALS ON INTERFACIAL RHEOLOGICAL PROPERTIES OF OIL/WATER SYSTEMS

István Lakatos, Julianna Lakatos-Szabó

Research Laboratory for Mining Chemistry, 3515 Miskolc-Egyetemváros, P.O. Box 2, Hungary

Although the effect of interfacial tension and wettability on efficiency of different industrial processes was recognized many decades ago and the formation of rigid films at water/oil interfaces was also firmly proved, the role of interfacial rheology in relevant topics was practically neglected until now. However, recently an extensive research activity connected with the enhanced oil recovery, pharmaceutical,

food and surfactant industry, etc. laid repeatedly stress upon interfacial rheological behaviour of oil/water systems. Therefore, the main objective of the research programme was to demonstrate that the interfacial rheological properties (viscosity, non-Newtonian flow behaviour, constants of the different rheological models, temperature dependence of viscosity, the activation energy of the viscous flow, etc.) are sensitive parameters for interfacial characterization of oil/water systems containing inorganic electrolytes and alkaline materials. The measurements were carried out with Contraves Low Shear 30 rotational viscometer using a biconical bob. The flow curves were recorded between  $10^{-3}$  and  $10^2 \text{ s}^{-1}$  shear rates and in temperature range of 303-343 K. A characteristic Hungarian crude oil was used as model in order to demonstrate the great variety of interfacial rheological properties in the presence of NaCl, NaOH and Na-silicates.

The detailed laboratory studies definitely proved that the interfacial rheological properties are extremely sensitive parameters towards the chemical composition of the aqueous phase. The general observations can be summarised as follows:

1. The inorganic electrolytes have negligible effect on interfacial viscosity of oil/water systems. Their effect remains usually within one order of magnitude, while in presence of alkaline materials the IFV may decrease by orders of magnitude and it might be as low as 0.1 mNs/m.
2. The alkaline materials suppress the non-Newtonian flow behaviour: at short contact time the interfacial layers show practically Newtonian character.
3. The viscosity decreasing effect and suppression of the structural viscosity (plasticity) increases with the concentration. Apparently, the effect ensues, however, at a certain concentration, which is roughly 1 g/l.
4. The effect of temperature on interfacial rheological properties is dominant only at low alkali concentrations and long contact times. But, at high alkali content, and particularly at low shear rate, the effect of temperature is negligible.

The effect of tested chemicals are interpreted by chemical reactions in the boundary layer and the modification of the dissociation equilibrium of the adsorbed natural surfactants being in the interface. The observations firmly proved that formation of emulsions is controlled primarily by the interfacial tension, while the coalescence of emulsion is controlled primarily by the interfacial viscosity. The experimental results provided conclusive evidences that the interfacial rheology is an efficient and powerful detection technique, which may enhance our knowledge on formation, structure, properties and behaviour of interfacial layers. Thus, it will probably accelerate significantly the progress in all areas of oil field chemistry, colloid chemistry and the relevant industrial technologies.

## 769.G3 RHEOLOGY OF CONCENTRATED OIL IN WATER EMULSIONS

**P. Manoj, A. Watson, A. Fillery-Travis, D. Hibberd and M. Robins.**

*Institute of Food Research, Norwich Research Park, Colney, Norwich NR4 7UA, UK*

In many successful formulations, the oil droplets (diameter 0.3-10  $\mu\text{m}$ ) in food emulsions of the oil-in-water type are flocculated by the presence of salts and/or polymers in the aqueous phase. The flocculated droplets form a network which extends throughout the container, and if strong enough, may hold the droplets in suspension.

In this work, we have characterised the rheological properties of these flocculated networks. Measurements of the complex rheological properties have been carried out on emulsions (bromohexadecane oil dispersed in Hydroxyethylcellulose (HEC) polymer aqueous phase) utilising the viscomerry and creep modes of our Bohlin CS Controlled Stress rheometer with a double gap geometry.

With the absence of zero-shear viscosity, the shear/stress/shear rate behaviour (non-linear flow curve) of the emulsions was described by Casson's model. The yield-stress of the emulsions was found to depend on the concentrations of the dispersed phase (oil) and the polymer. The yield stress of the emulsions increased non-linearly with the dispersed phase and polymer concentration.



## 770.G3 INFLUENCE OF THE AQUEOUS MEDIUM ON THE VISCOELASTIC PROPERTIES OF NaCMC, HPMC AND THERMALLY PREGELATINIZED STARCH GELS

V. Mihailova<sup>1</sup>, St. Titeva<sup>1</sup>, R. Kotsilkova<sup>2</sup>, E. Krusteva<sup>2</sup>, E. Minkov<sup>2</sup>

<sup>1</sup>Faculty of Pharmacy, Medical University, Sofia, Bulgaria

<sup>2</sup>Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Sciences, Sofia, Bulgaria

Neutral and semisynthetic hydrophilic polymers are widely used in pharmaceutical technology for formulating controlled release drug delivery systems. The behaviour of the gelled layer, formed around the hydrophilic matrices after water uptake is of major importance for the drug release profiles. Viscoelastic properties are related to gel structure, interchain interaction and entanglements, erosion and drug diffusion processes. This imposes the rheological measurements as a reliable and suitable approach to the characterisation of the polymeric network structure. Oscillatory test parameters were observed for highly concentrated Na carboxymethyl cellulose (NaCMC), hydroxypropylmethyl cellulose (HPMC) and thermally pregelatinized starch hydrogels using Rheotron Brabender rheometer with cone-plate geometry of the measuring device. The hydrogels were obtained by swelling of matrix tablets in 0.1 N HCl solution (pH 1.0 and in pH 6.8 phosphate buffer. The gel concentration range was between 15 and 30 % w/w. All measurements were carried out at a temperature of  $37 \pm 0.5^\circ \text{C}$ . The storage ( $G'$ ) and the loss ( $G''$ ) moduli, as well as the tangent of the phase angle were obtained under dynamic conditions of non-destructive oscillatory tests in the frequency range of 0.01 and 4.0 Hz and an attempt is made to determine the relaxation time spectra on the basis of these parameters.

The pH and the ion type of the environment exert an influence on both the elastic and viscous behaviour of the NaCMC gels. The viscous character of the polyelectrolyte gel is pronounced in the phosphate buffer, while the elastic nature is dominating in the acidic medium due to the polymer neutralization. The sensitivity of neutral HPMC gels to pH changes is insignificant. No considerable differences of the functional parameters  $G'$ ,  $G''$  and  $\tan \delta$  depending on the ionic strength have been found.

The viscoelastic behaviour of the pregelatinized starch gels is very similar to that of the neutralized NaCMC ones, regardless of the used media. This suggests a porous gel system in which the channels are with fixed inert matrix-like geometry.

## 771.G3 SHEAR INDUCED ALIGNMENT AND TEXTURES IN A MICELLAR CUBIC CRYSTAL

François Molino<sup>1</sup>, Jean-François Berret<sup>1</sup>, Grégoire Porte<sup>1</sup>, Olivier Diat<sup>2</sup> and Peter Lindner<sup>3</sup>

<sup>1</sup>Groupe de Dynamique des Phases Condensées, U.M.R. CNRS 5581, Université de Montpellier II, F-34095 Montpellier Cedex 05, France

<sup>2</sup>European Synchrotron Radiation Facility, BP 220, F-38042 Grenoble Cedex, France

<sup>3</sup>Institut Laue Langenvin, BP 156, F-38042 Grenoble Cedex 9, France

We report small-angle neutron (SANS) and x ray (SAXS) scattering experiments under shear on a micellar cubic crystal. The micelles results from self-assembling of triblock copolymers  $(\text{EO})_{127}(\text{PO})_{69}(\text{EO})_{127}$  dissolved in water, where EO is for ethylene oxide and PO for propylene oxide. At concentration above 20 %, the spherical aggregates (120 Å radius) come to a close packing, forming a long range ordered cubic phase. We first show that the solid elastoplastic samples are polycrystalline at rest, with a symmetry in agreement with fcc structure (lattice parameter  $a = 313 \text{ Å}$ ). Under shear, the samples flow above the yield stress, and the polycrystalline texture undergoes a shear alignment process: the isotropic rings related to the initial powder-average transform into well defined Bragg peaks. The intensity and distribution of these Bragg peaks (26 have been detected) in the reciprocal space are consistent with a layering of the cubic crystal into 2D-hexagonal compact layers with the (110) directions parallel to the flow velocity. The scattering patterns, as received from SANS and SAXS evolve markedly upon increasing the shear rate applied and the corresponding shear-induced structures are discussed and related to the mechanical responses obtained from nonlinear rheology.



## 772.G3 COMPARISON OF THE DYNAMIC BEHAVIOUR OF PROTEIN FILMS AT AIR-WATER AND OIL-WATER INTERFACES

**Brent S. Murray**

*Food Colloids Group, The Procter Department of Food Science,  
The University of Leeds, Leeds LS6 9JT, UK*

Spread and adsorbed films of pure milk proteins  $\beta$ -lactoglobulin and  $\beta$ -casein have been examined at the oil-water interface (the oil being n-tetradecane) and at the air-water interface. The rates of protein adsorption and desorption have been considered and also the response of the protein films the dilatational and shear deformations. Evidence is presented that protein conformation at the two types of interface may be quite different. Films appear to be more unfolded at the oil-water interface, but not necessarily less mobile, than at the air-water interface. At the air-water interface films behave as if in a more insoluble, aggregated state. When there are more cross-linking interactions between the molecules in the unfolded protein films this leads to large increases in the viscosity and elasticity of the films, with implications for emulsion and foam stability.

## 773.G3 CORRELATION BETWEEN EMULSION AND FOAM STABILITY AND INTERFACIAL AND SURFACE RHEOLOGY

**Robert Orr<sup>1</sup>, Brita Blörstad<sup>1</sup>, Alain Cagna<sup>2</sup>, and Bernard Delorme<sup>2</sup>**

<sup>1</sup>*The Research Centre, Norsk Hydro ASA, PO Box 2560, N-3901 Porsgrunn, Norway*

<sup>2</sup>*Interfacial Technology Concept, Parc de Chancolan, F-69770 Longessaigne, France*

Crude oil contains natural surfactants and these can cause separation and flow problems by forming emulsions and foams. For example this necessitates the use of demulsifiers and defoamers before the oil/water/gas separator for some crude oils.

It has long been recognised that surface/interfacial rheological can be the cause of the stabilisation of foams/emulsions. In this work we have studied two surfactants, one which forms elastic surfaces (Teepol) and one which forms viscous surfaces (stearoyl-2-lactylate). Different concentrations of the surfactants were studied. The non-equilibrium rheological properties of the two surfactants for water-air and water-paraffin interfaces were measured by the oscillation drop tensiometer (ODP)<sup>1</sup> and the equilibrium properties by both the ODP and the ring trough method (RTM)<sup>2</sup>. Results were compared with data for emulsion/foam stability and drop size.

A further such comparison was made for a crude oil/formation water system with different concentration of demulsifier.

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## 774.G3 RHEOLOGICAL PROPERTIES OF MONTMORILLONITE AQUEOUS DISPERSIONS WITH PHOSPHATIDES

**S.V. Pakhovchyshyn, V.F. Grytsenko, O.V. Bacherykov**

*Institute of Surface Chemistry, National Academy of Sciences of Ukraine, Prospekt Nauky 31,  
Kyiv, 252028 Ukraine*

The influence of phosphatide concentrate emulsions upon rheological properties of concentrated aqueous montmorillonite dispersions is discussed. Na-form of Cherkassky montmorillonite and phosphatide concentrate of sunflower oil containing mainly lecithins and phosphatidylethanolamines with sunflower oil were chosen for investigation. Adding 2 wt.% of phosphatides results in decreasing intensity of mechanical energy dissipation in montmorillonite dispersions per unit time providing the flow in a unit volume. It is shown using electrophoresis, rheological data and IR-spectroscopy that phosphatides adsorption on

montmorillonite particles surface results in decreasing interparticle interaction in filtration cakes and in improvement of lubricating properties of drilling muds. Mechanism of interaction of montmorillonite surface with phosphatide concentrate is proposed. Fractal analyze techniques have been effectively employed to investigate the difference between stable and unstable dyspersed systems.

### **775.G3 INFLUENCE OF REDUCED-CHOLESTEROL YOLK ON THE VISCOELASTIC BEHAVIOUR OF CONCENTRATED O/W EMULSIONS**

**A. Paraskevopoulou<sup>1</sup>, V. Kiosseoglou<sup>1</sup>, S. Alevizopoulos<sup>2</sup> and S. Kasapis<sup>2</sup>**

<sup>1</sup>*Laboratory of Food Chemistry and Technology, Faculty of Chemistry,  
Aristotle University of Thessaloniki, 54 006, Greece*

<sup>2</sup>*Department of Food Research and Technology, Granfield University, Silsoe College,  
Silsoe, Bedfordshire, MK 45 4DT, U.K.*

A stress-controlled Carri-Med rheometer was used to carry out dynamic oscillatory and creep compliance experiments within the linear viscoelastic region on mayonaise emulsions prepared with low-in-cholesterol egg yolk protein concentrates. Spray-dried egg yolk as well as yolk protein concentrates prepared by extracting with petroleum ether, petroleum ether/ethanol, ethanol/water, or supercritical carbon dioxide were used. The type of egg product varied, while the composition of the emulsions was held constant. The method of lipid extraction influenced both the emulsion droplet size and the viscoelastic parameters. The small deformation properties of the emulsions are interpreted in connection with the interdroplet interactions as they are affected by the presence of yolk protein concentrates.

### **776.G3 BROWNIAN MOTION OF MICROPARTICLES AT LIQUID-GAS INTERFACE**

**B. Radoev, M. Avramov, B. Cohen, and E. Manev**

*University of Sofia, Department of Physical Chemistry, 1126 Sofia, Bulgaria*

Brownian motion is employed here as a tool for studying the rheology of liquid-gas interfaces in the presence of surfactants. Brownian motion of glass microspheres (~1  $\mu\text{m}$  size) at water-air interface in the presence of surfactants (DDA, CTACH, and CTAB) is directly measured with the use of an image analysing method. The most interesting finding is that above CMC Brownian motion becomes non homogeneous, indicating heterogeneous adsorption distribution of both soluble and insoluble surfactants. This hypothesis is supported by the diffusion coefficient values as well. Above CMC diffusion coefficients are lower (in contrast to the model of homogeneous adsorption) and, what is more symptomatic, the experimental data here are statistically more dispersed, compared with the data below CMC.

The theoretical analysis is made from the view-point of the Nernst-Planck-Einstein approach relating the particle diffusion coefficients to their mobility. Special attention is paid to the role of surfactants in the dynamics of the process. It is shown that due to the coupling between fluxes taking place at the surface and in the bulk, Brownian motion of floating particles should exhibit some nontrivial features in its behaviour. In the case of insoluble surfactants, for example, the mobility of particles is not a constant, as it is in the bulk, but depends on their velocities (a system with non-linear response).

### **777.G3 THIXOTROPIC FLOW OF THE CRUDE OIL: INTERPRETATION OF HYSTERESIS EFFECTS IN TERMS OF THE MODIFIED CASSON'S MODEL**

**S.V. Remizov, I.L. Volchkova, E.A. Kirsanov and V.N. Matveenko**

*Moscow State University, Moscow, Russia*

Flow curves of the highly paraffinaceous oil are often observed to constitute hysteresis loops. We have established that both the up-curve ( $\uparrow$ ) and the down-curve ( $\downarrow$ ) may be adequately fitted by the Casson's

equation  $\tau^{1/2} = \tau_c^{1/2} + \eta_c^{1/2} \dot{\gamma}^{1/2}$  within the highshear rate range. Hysteresis may be characterized by the difference between the dynamical limiting shear stress values referred to the up-curve and the down-curve, respectively, i.e.  $\tau_c^\uparrow > \tau_c^\downarrow$ . In order to consider the thixotropic effects, we have modified the Casson's microrheological model, supposing the average size of the flow units ( $j^\downarrow$ ) related to a down-curve is less than that of an up-curve ( $j^\uparrow$ ) at the same shear rate ( $\dot{\gamma}$ ), due to the lag of the flow units joining. We have shown, that if condition  $j^\downarrow = m_j^\uparrow$  is valid, then,  $\tau_c^\downarrow = m^2 \tau_c^\uparrow$ , where  $m$  is parameter, independent of  $\dot{\gamma}$ . Values of  $m$ , calculated from experimental data  $\tau_c^\uparrow$ ;  $\tau_c^\downarrow$  are in good agreement with the theoretically predicted interval ( $213 < m \leq 1$ ).

## 778.G3

### IN SITU DEUTERIUM NMR STUDIES OF SHEARED SURFACTANT/WATER SYSTEMS

Claudia Schmidt and Stefan Müller

*Institut für Makromolekulare Chemie, Universität Freiburg, Sonnenstr. 5, D-79104 Freiburg, Germany*

Mixtures of surfactants and water show a rich polymorphism. With increasing surfactant concentration several liquid crystalline phases may be found. These complex fluids show interesting rheological behavior. For its understanding it is important to measure not only macroscopic properties, but also, on a microscopic scale, molecular orientation and phase structure during flow. In the past, primarily optical methods have been combined with rheological measurements. Here, we present a different approach, using deuterium NMR spectroscopy to provide the desired microscopic information.

The quadrupole coupling of the deuterium nucleus is a convenient probe for the investigation of molecular orientations in solids and anisotropic liquids. Deuterium NMR has been used for many years to study the equilibrium properties of thermotropic and lyotropic liquid crystals. The investigation of aqueous lyotropic liquid crystals by this method can be performed on mixtures enriched with D<sub>2</sub>O, thus requiring no synthetic effort for isotopic labeling.

We demonstrate that NMR can be used to study the complex flow behavior of lyotropic liquid crystals in situ. For the measurement of NMR spectra during shear, we designed different cells that are integrated in conventional probe heads for a wide-bore superconducting magnet [1,2]. Both cone-and-plate [1] and Couette geometries [2] have been used.

We have concentrated our studies on the lamellar [3] and the hexagonal [2,4] phases of aqueous solutions of the nonionic oligo(ethyleneoxide) alkyl ethers (C<sub>n</sub>E<sub>m</sub>, where C<sub>n</sub> denotes all alkyl chain of length  $n$  and E<sub>m</sub> an oligo(ethylene oxide) chain of  $m$  units). For the lamellar phase of C<sub>12</sub>E<sub>4</sub> two of three states of orientation during shear, described previously [5], can be identified by NMR [3]. We find one state at low

shear rates ( $\dot{\gamma}$ ), in which the lamellae are preferentially parallel to the velocity-vorticity plane, and another state at higher shear rates, which can be considered as a defect structure consisting of either a net of disclination lines or of a close packing of multilamellar vesicles [5]. The formation of the latter state is suppressed when the surfactant molecules are attached with their hydrophobic end to a polymer chain, forming a polymer surfactant.

Our rheo-NMR studies of the hexagonal phase show that the director becomes aligned parallel to the flow direction [2,4]. If small shear rates of the order of 10<sup>-3</sup>s<sup>-1</sup> are applied, the process of reorientation can be followed by NMR. The reorientation depends on the shear strain  $\gamma = \dot{\gamma} t$  [2]. For a monodomain with the director initially aligned parallel to the velocity gradient we could show that shear causes a solid-like reorientation by tilting the director by an angle  $\theta = \arctan \gamma$  [4]. In addition, prolonged shear causes the amplitude of undulations, observable by optical microscopy [4,6], to decrease significantly.

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## 779.G3

TIME PERIODIC CHANGES OF VISCOSITY IN  
CONCENTRATED KAOLIN SUSPENSIONS

O. Seidel, F. Bagusat, H.-J. Mögel

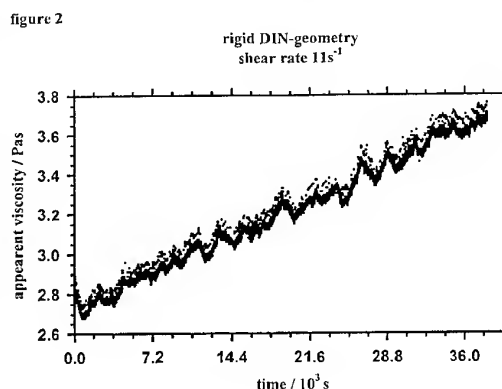
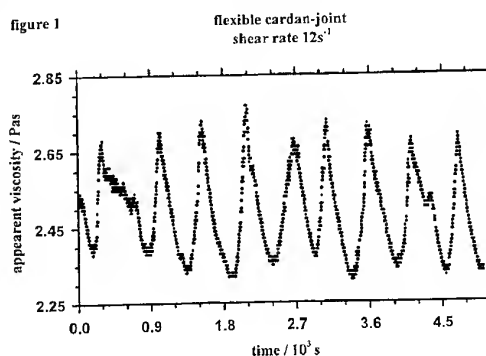
Freiberg University of Mining and Technology, Institute of Physical Chemistry, D-09596 Freiberg, Germany

Rheologic investigations of slurry kaolin suspensions have been made with an air bearded searle type rotational viscosimeter. The suspensions have 30 % solid mass content of kaolin in a 0.5 M NaSCN-solution with pH=11. Applying a constant shear rate (in a small interval of about  $10 \text{ s}^{-1}$ ) and a constant temperature (293 K), viscosity time curves as shown in figures 1 and 2 were obtained. A time periodic behaviour for the measured signal, henceforth referred to as oscillation effect, is clearly expressed in figure 1, but is evident from figure 2 as well. Comparative experiments with calibration oil instead of kaolin suspensions imply a suspension induced contribution to the oscillation effect.

Experiments with kaolin suspensions using a flexible linked inner cylinder show that the inner cylinder is dislocated away from its centered position. It arrives at a maximum deviation and subsequently relocates to its former coaxial position. This process performs periodically (O. Seidel, *Non newtonian behaviour of kaolin suspensions*, diploma theses, Freiberg, 1995). The higher the decentration of the spindle, the higher must be the torque of the apparatus at constant shear rate. Because of the proportionality of the measured viscosity and the torque, the periodicity in figure 1 is explained.

Using rotational viscosimeters from various vendors and geometries, the oscillation effect has been found. For example, figure 1 shows the oscillation effect for fixed geometry measurements. While applying high shear rates or pauses within the same experiment, it is not shown any destructive influence to the appearance of the oscillations after returning to original conditions. In case of using the flexible linked inner cylinder, the oscillation effect is assumed to be caused by local, anisotropically distributed inhomogeneities, which originate from shear induced agglomeration and deglomeration of suspended particles. The oscillation effect which appears by using a rigid spindle connection could possibly caused by agglomeration and deglomeration processes in the bulk.

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## 780.G3

PARTICLE INTERACTION AND RHEOLOGICAL PROPERTIES  
OF SUSPENSIONS OF TITANIUM DIOXIDE, KAOLIN AND WOLLASTONITEM.M. Soltys<sup>1</sup>, V.P. Zakordonskiy<sup>1</sup>, S.G. Croll<sup>2</sup>, Z.M. Yaremko<sup>1</sup>, I.M. Krupak<sup>1</sup><sup>1</sup>I. Franko Lviv State University, Kyrila & Mephodia str., 8 Lviv, 290005 Ukraine<sup>2</sup>SCM Chemicals, Technical Center, 3901 Fort Armistead Road, Baltimore, Maryland 21226-1899 USA

Aggregation sedimentation stability and rheological properties are parameters of dispersed systems that determine their usefulness in practical applications. Therefore, measurement of these properties and their inter-relationships are problems worthy of study. Results on the rheological behaviour of aqueous suspensions of titanium dioxide, kaolin and wollastonite are reported in this paper. Effects of solid phase concentration and the addition of surfactants, ionic Atlas G3300 and non-ionic Triton X-100, were studied. The data are discussed within the framework of a cell model of viscosity that accounts for the long-range surface forces between particles. Further, estimates were made of the minimum energy potential that is necessary for preventing (or breaking up) coagulation and of the maximum possible volume fraction of

solids in each of the systems. This approach also allowed an estimate of the attractive force between particles and thus the appropriate Hamaker constants for titanium dioxide, kaolin and wollastonite.

### 781.G3 INTERFACIAL DILATIONAL PROPERTIES OF SURFACTANT SOLUTIONS

**Wantke, K.-D., and Fruhner, H., Lunkenheimer, K.,**

*Max-Planck-Institut für Kolloid- und Grenzflächenforschung Berlin/Teltow, Germany*

The specific problems of the interfacial rheology of surfactant solutions result from the fact that the adjacent bulk phase (air/fluid) is an incompressible, homogeneous fluid and a fluid interface can be considered as a two-dimensional, strong compressible phase with varying components. In a static state the composition is determined by the laws of equilibrium thermodynamics. An external disturbance by deformation or heating leads not only to a new tension state but also to a nonequilibrium state of the system which causes relaxation processes in the subsurface and in the surface.

Therefore, the introduction of an independent two-dimensional tension state is an unrealistic idealization. However, the formal use of a two-dimensional tension tensor is correct if the influence of the adjacent bulk phase is taken into account by additional terms in the force balance. It is then possible to describe the rheological processes at the surface by a divergence equation of a tension tensor.

For the experimental prove of the theoretical models a special device, a new version of the oscillating bubble method was developed. With this apparatus we can measure the dilational rheological properties of the surface in a frequency range 0.5 - 500Hz with a relative deformation rate of 0.1 [1]. The measured parameter value is the "effective" elasticity of the fluid interface which is determined by elastic, viscous and transfer properties. Contrary to a clean water surface, which has no surface elasticity or surface viscosity, a surfactant solution like a soap solution may exhibit both properties. By extension of the frequency range over 100Hz it is possible to demonstrate in a clear manner the appearance of an intrinsic viscosity for special solutions which are independent of the transfer effects. It can be interpreted as a consequence of the inhomogeneous structure and dynamics of the system near the surface. Using these new experimental results we can show that a rapid growth in the stability of foams correlates with an increase of the intrinsic surface viscosity of the surfactant solutions. In addition, the improved method has the potential for detailed experimental investigations of several unsolved problems of dynamic processes near the fluid interfaces, like molecular exchange between the interface and the bulk phase and the force balance by disturbed thermodynamic equilibrium. The preliminary results indicate a need for new theoretical models.

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### 782.G3 CONTROL OF RHEOLOGICAL AND MECHANICAL PROPERTIES OF HETEROGENEOUS POLYACRYLATE MIXTURES

**D.N. Yemelyanov, V.A. Myachev**

*Nizhny Novgorod State University, Nizhny Novgorod, Russia*

The mechanical properties of composite heterogeneous polymer materials are determined to a great extent by the morphology of a system, surface interfacial interaction and compatibility of components.

One of methods of the interfacial interaction control is based on the modification of properties of a dispersed phase due to the variation of the copolymer composition, introduced to a polymer matrix. Thus, the improvement of impact strength of polystyrene and polymethylmethacrylate can be achieved by addition to them of elastomeric components resins. The compositions formed, however, become opaque because these polymers are practically incompatible. The improvement of impact strength, while preserving a transparency of a polymethylmethacrylate organic glass, arises from the formation of dispersions having a phase of acrylic copolymers of a certain composition. Simultaneously the dispersed phase can act as a polymer plasticizer and control rheological properties and processibility of mixture melts.

The transparency of heterogeneous compositions was brought about by close refractive indexes of components by controlling, the composition and preparation conditions of copolymers-modifiers as well as the morphology of component distribution.

The preparation of mixtures was carried out by various methods that influenced in some way the morphology although affected little viscous-mechanical properties of systems. In the process of polymerization filling the starting reaction systems - solutions of copolymers in methylmethacrylate - converted to mixtures in the course of the reaction. In other cases, the mixtures were formed by mixing of polymer components through a solution or a melt.

### 783.G3

#### THE RESEARCH OF RHEOLOGICAL PROPERTIES OF PARAFFIN-CONTAINING DISPERSE SYSTEMS

Yui Tsun-sin T., Musabekov K.

*Al-Faraby Kazakh State National University, Almaty, Kazakhstan*

The colloid-chemical condition of oil systems is characterized by range of specific interactions between oil components and oil products which can be related to intermolecular interactions. As a result of the intermolecular interactions there are a structure formation processes. The structure formation processes lead either to division into layers of oil system, or to their stabilisation owing to covering the globules surface by the substances with properties of depressor attachments. The research of the paraffin containing systems structure-mechanical properties at lowered temperatures conditions and when the depressor attachments are used allows to analyse more deeply the mechanism of structure-formation in the time of the new phase of paraffin appearance and development from over saturated solutions. In this work the influence of the paraffin deposits inhibitor XT-48 and oil-soluble surface-active substance OP-4 on the structure-mechanical properties of natural dzetibaiskaja and karadzanbaskaja oils was studied. It was shown that the researched oil systems structure-mechanical properties at the introduction of the XT-48 and OP-4 have an extreme character. There were found the concentrations of additions at which the structure-mechanical constants and characteristics of karadzanbaskaja and dzetibaiskaja oils decrease. It was determined that for improvement of the investigated oils reological properties at the lowered temperature (0-5°C) it needs the increasing of the additions XT-48 and OP-4.

### 784.G4

#### ORDER OF THE PHASE TRANSITION LIQUID EXPANDED-LIQUID CONDENSED PHASE OF INSOLUBLE MONOLAYERS

I. Bivas<sup>1</sup>, I. Panayotov<sup>2</sup>

<sup>1</sup>*Institute of Solid State Physics, Bulgarian Academy of Sciences,  
Laboratory of Liquid Crystals, 72 Tzarigradsko chaussee blvd., Sofia 1784, Bulgaria*

<sup>2</sup>*Sofia University, Department of Chemistry, Chair of Physical Chemistry,  
1 J. Bourchier blvd., Sofia 1126, Bulgaria*

If two phases of an insoluble monolayer coexist and one of them is dispersed into the other in form of small aggregates, the lateral pressure of the system should change due to the fragmentation. We propose an expression for the free energy of a monolayer, consisting of some condensed phase floating in form of circular monodispersed "icebergs" in the expanded one. The free energy is minimized with respect to the number of molecules per aggregate (this is an internal parameter of the system). From this condition the number of molecules in one aggregate is calculated as a function of the mean area per molecule in the monolayer. In the liquid expanded phase this number is equal to one. In the region of the phase transition it can be finite. In such a case the plateau in the  $\Pi$ - $a$  isotherm of the system is not horizontal. The size of the aggregates and the tilt of the plateau crucially depend on the edge energy of the one-dimensional interface between the two phases. As a result, another picture of the phase behavior of the monolayer can be proposed. A given mean area  $a^*$  per molecule exists with the property that if the mean area per molecule  $a$  is greater than  $a^*$  the number of molecules in the aggregates (nuclei) of the condensed phase in the expanded one is equal to one, while at  $a < a^*$  the nuclei contain more than one molecule. At  $a = a^*$  a phase transition of second order appears. The inclined plateau is not a region of coexistence of two phases, but one phase consisting of the liquid expanded continuous phase containing aggregates of the condensed one. The number and size of the aggregates is a function of the mean area per molecule in the monolayer.

Our model proposes a possibility to remove some of the existing contradictions between the experimental observations and the theoretical requirements in the phase behavior of the monolayers.

#### **785.G4 ABOUT DYNAMICS OF RUDE-DISPERSED GAS ENIULTION FORM DURING OIL AND GAS ARTIFICIAL RECOVERY BY SURFACTANTS**

**Carimov M.Ph., Dolgov X.V., T.L. Dong, Tr.S. Phiet, N.V. Canh**

*Research & Design Institute for offshore Oil and Gas Production, Vietsovpetro J. V., Vietnam*

A mathematical model bubble form and development during gas flow seepage into fluid through the gaslift valves is offered. This model takes into consideration the dynamics of surface tension change at the gas-liquid interface. Fluid contains dissolved surfactants. Surface tension is changes, depending on adsorption of surfactant molecule, mass transfer is considered in Diffusion approximation under the conditions of volume (Archimed force) and surface (hydrodynamic) forces on the variable gas mass. A differential equation is obtained which is analogous to Metschersky-Levy-Civita one. Equation solution allows to calculate the dimension and critical velocities of bubble form. Solution analysis is used to work out-quantitative requirements to the surfactant selection in oil and cas production stimulation. The experimental test of the obtained theoretical results has been confirmed on Rebinder R. A.s unit.

#### **786.G4 CONCENTRATION-DEPENDENT SEDIMENTATION OF FERROFLUIDS AND MAGNETIC SILICA DISPERSIONS**

**Liesbeth N. Donselaar and Albert P. Philipse**

*Van't Hoff laboratory for Physical and Colloidal Chemistry, University of Utrecht,  
Padualaan 8, 3584 CH Utrecht, The Netherlands.*

We present the results of sedimentation experiments with a recently developed magnetic colloidal system. The colloids consist of three layers. On a superparamagnetic maghemite core a silica layer is precipitated. Then the particles are sterically stabilised by grafting with a polymer. Stable discrete colloids are obtained, dispersed in a non-aqueous solvent. With the non-magnetic shell the effect of the magnetic interaction between the particles can be adjusted. This magnetic interaction can be investigated with sedimentation experiments. The sedimentation of magnetic particles has been studied as a function of the concentration and the silica shell thickness, using gravitational settling as well as ultracentrifugation. Batchelor has shown that the mean settling velocity  $U$  in a dilute dispersion of non-magnetic spheres with volume fraction  $\phi$  is  $\frac{U}{U_0} = 1 - K\phi$ , with  $U_0$  the sedimentation velocity at infinite dilution and  $K$  a constant. For

hard sphere colloids  $K$  was calculated theoretically to be 6.55. We found that by decreasing the silica layer thickness  $K$  decreases and even may become negative. The increase in sedimentation velocity at higher concentration (due to a negative  $K$ ) seems not to have been observed earlier in colloidal dispersions, and can be explained with a recent theory for sedimentation of paramagnetic spheres [J. Dhont, "An introduction to dynamics of colloids", Elsevier, 1996].

#### **787.G4 DYNAMICS OF CONFINED VISCO-ELASTIC LIQUIDS: RUPTURE OF THIN LIQUID FILMS**

**L.J. Evers and G. Frens**

*Laboratory of Physical Chemisity, Delft University of Technology, Julianalaan 136,  
2628 BL Delft, The Netherlands*

Investigations on the bursting of vertical thin liquid films stabilized by surfactants have been carried out. The use of high speed flash photography enables us to determine the bursting velocity. A hole in the soap film is created by an electrical spark and expands in the liquid sheet. In onc single photo the evolution

of this hole can be followed in time. Analogies in bursting behaviour of ultra thin films from a Newtonian solution (Newton-black films) and films from a visco-elastic surfactant solution led to a physical model which describes the bursting of visco-elastic liquid films. Usually, the bursting of liquid films from Newtonian solutions is characterized by a constant rupture velocity. In both experiments, with Newton-black films and with 'gel' films, we find a retardation of the bursting process. Therefore, the time dependence of the rupture velocity as the hole in a liquid film grows seems to be characteristic for visco-elastic systems. This retardation becomes more pronounced when the film gets thinner than a certain critical thickness.

It is deduced that the plateau elasticity modulus increases when the film thickness is below the characteristic mesh size in a molecular gel which exists in the liquid lamella. Rupturing films, drawn from a visco-elastic CTAB/decanoic acid solution show an increase in elasticity modulus when the film becomes thinner than 100 nm. In Newton-black films the characteristic length scale is of molecular dimensions.

## 788.G4 THE RESEARCH ON APPLICATION OF RARE EARTH TO SURFACE CHEMICAL HEAT TREATMENT OF HOT-WORKING DIE STEELS

Hu Zhengqian, Zhang Wenhua, Yao Anyou

*School of Mechanical and Electrical Engineering, Wuhan University of Technology, Wuhan, P. R. China*

The application of rare earth (RE) to the surface treatment of steels has been a new problem to study since the end of 1960s. At present the research is still in the stage of accumulating experimental materials as well as summing up objective law, far from forming a complete and systematic theory. Recent years' study shows that for steel surface chemical heat treatment, besides the possibility of increasing steel surface activity and adsorption effect on diffused atoms, RE can also be micro solid dissolved, i.e. microalloyed in steels. All this might have effect on catalytic diffusion and also an improvement on diffused layer's capabilities.

This paper studies a compound treatment, i.e. liquid S, N, C co-diffusing with RE and then oxidation, for hot-working die steels, and the effect of RE to thermal fatigue behavior of the diffused layer. XRD and SEM energy spectrum prove that trace RE element actually penetrates into the surface layer of steels.

The result shows that RE can reduce the gradient of change of hardness in diffused layer, improve the morphology and distribution of compounds, and reduce the degree of surface alligator crack for thermal fatigue. The behavior of thermal fatigue of hot-working die steels is raised by 70% or so because of the application of RE. The effect of RE is analysed according to the theory.

## 789.G4 EFFECT OF SURFACTANTS ON FRACTURE OF LIMESTONE

N.I. Ivanova, E.D. Shchukin

*Colloid Chem. Dept., Chem. Faculty, M.V. Lomonosov, Moscow State University, 119899 Moscow, Russia.*

The adsorption of surfactants from aqueous solution on solid surface, especially on minerals, is fundamentally important for many technical applications. In this study the effect of concentration of anionic, cationic and nonionic surfactants in aqueous solutions on some of mechanical properties (microhardness, grinding and drilling) of limestone was investigated. The change of adsorption density with surfactant's concentration depends on interaction between surface active substances and solid surface. For instance, the dense adsorption layer of anionic surfactant ABS (sodium alkylbenzenesulfonate) on hydrophilic surface of limestone are formed only at CMC concentrations of ABS. Contrary, in solutions of cationic surfactant CTAB (cetyltrimethylammonium bromide) the dense adsorbed layer are formed on surface of limestone at concentration, which at least is 100 times less than CMC. Effect of surfactants on the failure of solids is explained by Reh binder hypothesis.



## 790.G4

CORRELATION BETWEEN THE MICROFASE STRUCTURE  
OF SEGMENTED POLYURETHANE AND DISSIPATIVE PARAMETERSV.A. Lomovskoy<sup>1</sup>, V.K. Fuki<sup>2</sup>, T.T. Galaeva<sup>2</sup>, M.A. Severianova<sup>2</sup>, B.N. Tarasevich<sup>3</sup><sup>1</sup>*Institute of Physical Chemistry of Russian Academy of Sciences, Moscow*<sup>2</sup>*Joint Stock Company "Medicon LTD", Moscow*<sup>3</sup>*Moscow State University, Moscow*

Segmented polyurethane (SPU) in the phase divided system, consisting of united domains polar hard blocks (diisocyanate fragment) and polyoxytetramethylenglycol soft matrix. SPU structure alteration was determined by infrared spectroscopy and electron microscopy. Dissipative parameters were defined under investigation of the internal friction spectra. These spectra were registered using the free-vibration method in the frequency range 1 to 5 Hz under temperature interval 100-450 K. SPU-structure alteration was estimated by shift of absorption band maximum of carbonyl group. Carbonyl group has three absorption band maxima in SPU IR spectra under 1705 cm<sup>-1</sup>, 1724-1728 cm<sup>-1</sup>, 1735-1740 cm<sup>-1</sup>. The absorption band maximum in area 1705 cm<sup>-1</sup> relates to hydrogenous bond (H-bond) C=O...H-NH. Such H-bond enters hard block structure. The band maxima in areas 1724-1728 cm<sup>-1</sup> and 1735-1740 cm<sup>-1</sup> may refer to H-bonds of urethane group inside hard block or bond hard block with soft matrix. It was determined that possessing surface-active property oligomers and preliminary thermotreatment of SPU-polymer exert influence on the structure of investigated systems. Data in table 1 indicate transformations in IR-spectra of SPU-systems for temperature of structure formation 313 K and 343 K and for containing surface-active oligomer (SAO) and without it.

	SPU+SAO		SPU	
	313 K	343 K	313 K	343 K
% I (1705 cm <sup>-1</sup> )	63	49	45	43
% I (1724 cm <sup>-1</sup> )	16	25	21	22
% I (1735 cm <sup>-1</sup> )	21	26	34	35

Obtained data show that structure alterations are more essential for the systems containing surface-active substances than without it. These data are in accordance with results of electron microscopy. According to relaxation spectroscopy data thermotreatment temperature alterations result in shift of loss peaks along temperature axis.

## 791.G4 LOW-FREQUENCY COLLECTIVE VIBRATIONS IN DNA MACROMOLECULE

Dmitriy V. Moraru

UNITEC Ltd., Kyiv, Ukraine

Systematic theoretical modeling of DNA oligomers, carried out earlier by S.N. Volkov for the B conformation, is now extended to A- and melted DNA.

The mechanical model of infinite isolated DNA helix conformational mobility allowed to compute normal vibrations frequencies ( $\omega_i$ ) as well as to estimate their amplitudes ( $A_{ij}$ ) in a wide range of relative humidities (RH) and temperatures (T). The speed of sound along the helix axis ( $V_s$ ) was also calculated. DNA behaviour near the critical points of B-A transition or melting was studied introducing linear temperature dependence of model elastic constants. The effect of mass loading as the result of DNA hydration was taken into account.

The  $\omega_i$  obtained are in good accordance with experimental data, especially for lowest frequencies (16 cm<sup>-1</sup> for B-, 21 cm<sup>-1</sup> for A- and 28 cm<sup>-1</sup> for melted form). It was found that these frequencies correspond to base motions accompanied with strong deformations of hydrogen bonds. The possibility of base pair opening under this condition was pointed out. The  $V_s$  values are also traced the experimental results changing from 3.0 km/s (melted form) to 1.7 km/s (B-form).

It was shown that low-frequency vibrational spectra significantly depends on factors that influence on DNA conformation. The results obtained helped to explain the internal mechanics of DNA double helix and the extent to which external conditions influence on its behaviour. It is pointed out that some differences in low-frequency vibrational spectra between B and A double helices can affect on biological activity of DNA macromolecule.

## 792.G4

ENVIRONMENT INFLUENCE ON MECHANICAL  
PROPERTIES OF SOLIDS: QUANTUM-CHEMICAL APPROACHE. Nikitina<sup>1</sup>, A. Malkin<sup>1</sup>, and V. Khavryutchenko<sup>2</sup><sup>1</sup>*Institute of Applied Mechanics, Russian Ac. Sci., Moscow, Russia*<sup>2</sup>*Institute of Surface Chemistry, Nat. Ac.Sci. of Ukraine, Kiev, Ukraine,**Frank Laboratory of Nuclear Physics, Joint Institute for Nuclear Researches, Dubna, Russia*

The phenomenon of sharp decrease of solid strength in some environments is well known and finds many applications in various branches of engineering [1]. This event may be caused by different processes at the solids and surfactant interfaces. However, it is commonly accepted that the most obvious mechanism is decohesion - reduction of the interatomic bond strength of solid surface interacting with active medium. In this case we can speak about an activation of the mechanochemical reactions in the surface layers of solids interacting with environment particles under the mechanical stress. Quantum-chemical calculations based on cluster approximation seems to be the only way for the theoretical investigation of specific atom-scale mechanism of this phenomenon. In presented study a new mechanochemical approach of semiempirical quantumchemical AM1 method [2] was applied to modelling the mechanical behaviour of flumed silica and some organic polymers immersed in active media such as water solutions of some acid and base reagents, and some surfactant solutions. The computer simulation of surface deformation and fracture was performed for large clusters containing up to 160 atoms. The computational experiment consisted of sequential step-by-step deformations of clusters from the initial stable state to rupture. The complete optimisation of space structure was performed at each step. The alterations of the heats of formation, the changes in the structural and electronic configurations of the clusters, and the force characteristics of the systems in the process of deformation were obtained. It was shown that some acids and surfactant reagents have a great impact on Si-O-Si and C-C bond deformations and rupture and reduce the force necessary for the bond gap more than three times. Atom-scale mechanism of processes under study was discussed. The results of mechanochemical calculations were accompanied and verified by the vibration spectra analysis.

1. V.S. Yushchenko, T.P. Ponomareva, and E.D. Shchukin. J. Mat. Sci., 27, 1659 (1992)

2. V.D. Khavryutchenko, E.A. Nikitina, A.I. Malkin, E. Sheka, Phys. Low-Dimens. Struct., 6, 65 (1995).

793.G4 INTERFACIAL COMPOSITION AND INTERPARTICLE INTERACTIONS  
IN ALUMINOSILICATE SYSTEMS

Lioudmila A. Pavlova

*Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Kiev*

One of the main goals of materials science is to achieve high density by weakening the attractive interaction to a definite degree to provide still some cohesion and control the packing of particles in a perfect way. We studied mechanisms of interparticle contacts formation during coagulation to crystallization structures transformation in kaolinite and silicate glass dispersions and effect of surface modification on their physico-chemical and mechanical properties. The model of porous solids was used to characterize the parameters of the structures. Rheological behaviour of powder-like masses under load was observed. The number of surface active sites (SAS) of the kaolinite particles was studied by the method of IR-spectroscopy of adsorbed molecular probes. The protonic Brønsted (B) acidity was tested based on adsorbed pyridine spectra. The aprotic Lewis (L) acidic sites were tested with the aid of benzonitrile. The specific wetting heat and surface area were measured. The low and high molecular compounds were chemisorbed on the samples' surface in amount of 0.1-0.2 mass.% to modify it. The kaolinite-water interfacial interaction results in the adsorbed water film and B-type SAS formation on the surface of the disperse particles. The silicate glass-water interaction leads to the specific alkali poor gel-like layer formation with the higher gradient of  $C_{Na}$ . We assumed that the coagulation structure in kaolinite aqueous dispersions is caused by the origination of the interparticle bonds on account of acid-base interactions of Brønsted active sites. Water molecules depolymerize -Si-O-Si- glass network leading to SiOH formation. Neighbouring SiOH-groups react forming Si-O-Si and hydrogen bonds between the particles under external pressure. It contributes to the great excess of the silicate glass individual contacts strength over kaolinite ones. During the increase of temperature of

thermovacuum pretreatment the number of B-sites becomes less and structural parameters change strongly upon the temperature raising too. The origin of aprotic sites during thermal treating results in the enlargement of the contacts strength. The bonds formed could be the hydrogen, donor-acceptor and siloxane bonds up to 673 K. Simultaneously, the donor-acceptor bonding by acid-base recombination of aprotic sites occur and finally the latter becomes predominant as far as the temperature rises. Interfacial chemical composition and the interparticle interactions play the decisive role in the formation of spatial structures. Chemisorption of the silicoorganic liquids on the particles' surface of about 0,1 mass.% blocked the greater portion of active sites and lowered the hydrophilic properties significantly. The strength of the contacts was decreased to two orders of magnitude. The higher mobility of modified particles for the reason facilitated their forced overpacking and significantly more contacts were formed at identical pressures. Hard donor-acceptor and chemical bonds were formed in the sites of the contacts.

## 794.G4

### THE "CAMPHOR BOAT": AN EARLY FORM OF CHEMICO-MECHANICAL MOTION

Martin E.R. Shanahan

*Centre National de la Recherche Scientifique, Ecole Nationale Supérieure des Mines de Paris,  
Centre des Matériaux P.M. Fourt, B.P. 87, 91003 EVRY Cédex, France*

Over the last few years, great interest has been shown in physico-chemical mechanics, of which chemico-mechanical motion is an example. In particular Bain et al. in Oxford (1994) and Domingues Dos Santos and Ondarcuhu in Paris (1995) have conducted elegant experiments with "reactive drops", where a reagent within the drop reacts with the substrate, thus leading to reduced wettability on one side and consequent drop motion due to unequilibrated Young's forces.

We propose to analyze a much older case of the same basic phenomenon - that of the "camphor boat". A small piece of wood or polymer (celluloid) is cut in the form of a boat and a small piece of camphor, or solid soap, added at the stern. When placed on clean, still water (usually in the bath !), the reduced surface tension behind the boat due to contamination by the camphor/soap leads to motion of the boat. We analyze the situation and by comparing boat speed and contaminant spreading rate, calculate the critical size of the boat, for it to move spontaneously. Below a certain size, the boat will not go. If the surface of water is limited (the bath !), the boat finally stops due to the whole liquid surface being contaminated. We estimate the time required.

## 795.G4

### PHYSICAL-CHEMICAL MECHANICS IN STUDIES OF PETER A. REHBINDER AND HIS SCHOOL

Eugene D.Shchukin

*Moscow State University, Moscow 119899, Russia and the Johns Hopkins University,  
Baltimore, MD 21218, USA*

70 years ago, the effect of the strength decrease of solids caused by adsorption and interfacial energy lowering was discovered by P.A. Rehbinder: Physical-Chemical Mechanics was born - a new branch of the Surface and Colloid Science studying mechanical (structure-rheological) properties of disperse systems and materials in their dependence upon complex of physical-chemical factors, particularly, surface (interfacial) interactions. Some principal directions in these studies are mentioned here.

Effects of active media on deformation and fracture of all kinds of solids: metals, ionic and covalent bodies, molecular crystals, amorphous materials have been studied, principles of the medium action selectivity and kinetics of its spreading understood, molecular (dislocation) mechanisms elucidated using molecular dynamics simulation and *ab initio* quantum-mechanical calculations. The new phenomena have been disclosed: surface plasticization, reciprocal effect of solid and medium in heterogeneous catalysis, spontaneous dispersion and thermodynamically stable, lyophilic systems formation under conditions of the extremely low interfacial energy. These results serve as a basis in perfecting technology of rock drilling, grinding, hard materials treatment, and preventing the harmful media influence.

Physical-chemical investigations of the rheological properties of disperse systems and materials are developed. Elementary events of contact interactions between individual particles of disperse phases in various media have been experimentally studied; mechanisms of the coagulation (reversible) contacts transition to the phase ones (bridging of particles) have been explained in various technological and natural processes. Physical-chemical theories have been created of the strength of porous structures (catalysts, sorbents), of the entropic elasticity of thixotropic coagulation structures (drilling liquids). Complex investigations are provided of the rheological parameters and structure forming processes in the bulk phases and at the interfaces in biopolymer dispersions, foams, liquid-crystalline systems, and of the structure-rheological properties of the surfactant adsorption layers (strong stabilization factors), - as a general scientific basis of practical applications in many areas of industry and environment protection.

**796.G4****ELECTROPHORETIC DEPOSITION  
OF LATEX PARTICLES ON ELECTRODES****Y. Solomentsev<sup>1</sup>, M. Bohmer<sup>2</sup> and J. L. Anderson<sup>1</sup>**

<sup>1</sup>*Department of Chemical Engineering, Colloids, Polymers, and Surfaces Program,  
Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, USA*

<sup>2</sup>*Philips Research Laboratories Eindhoven, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands*

When latex particles about 10 microns in diameter were electrophoretically deposited onto a flat electrode at a low applied voltage, the formation of ordered clusters of particles was observed. When the polarity of the field was reversed, the particles remained on the surface because of the (stronger) gravitational field. However, the clusters broke up into singlets. The formation and breakup of clusters was reversible upon changing the direction of the field normal to the electrode.

A hydrodynamic model has been developed to describe long-range interactions between particles during electrophoretic deposition. The model predicts that the clustering of deposited particles is caused by electroosmotic flow about each particle, which tends to draw neighboring particles on the electrode closer to each other. Sample calculations for the relative velocity of two particles near an electrode are in semi-quantitative agreement with the experimental observations.

**797.G4****EXPERIMENTAL TEST OF THE CONVECTIVE MODEL OF  
CROSS-FLOW MICROFILTRATION****C.S. Vassilieff, T.A. Doneva**

*Laboratory of Biophysical Chemistry, Department of Physical Chemistry,  
University of Sofia, 1126 Sofia, Bulgaria*

The convective model accounts for the tangential mobility of the colloidal cake accumulating on the upstream surface of a membrane (or other) filter during cross-flow microfiltration. For sufficiently thin cake layers an approximate analytical expression relates the steady-state average filtration flux to the technological process parameters: transverse (transmembrane) pressure drop and longitudinal (tangential) shear rate (at the upstream surface of the dense cake supported by the membrane filter).

The specificity of the filtered suspension and cake is taken into account by means of their volume fractions and viscosities; the "filtration" specificity of the system is taken into account by means of the resistances of the membrane filter and the cake.

The convective model allows to use experimental transient cross-flow microfiltration data to prove or discard tangential mobility of the colloidal (as a rule pseudoplastic) cake. On the other hand steady-state microfiltration data can be used to estimate indirectly the specific filtration resistance and the non-Newtonian viscosity of the cake. Both quantities are also directly measurable: the former in a batch filtration experiment, the latter in rheological experiments.

A large set of experimental cross-flow microfiltration data (own and of other authors) are treated in this way yielding reasonable agreement between indirect estimates and independently measured values.

Predictions of the convective and other models are critically evaluated in a comparison with experimental data.

## 798.G4

INTERFACIAL INSTABILITY CAUSED  
BY HETEROGENEOUS CHEMICAL REACTION

A.V. Vyazmin, V.A. Kaminsky

*Karpov Institute of Physical Chemistry, Moscow, Russia*

The phenomenon of interfacial turbulence consists in the generation near interface of unordered convective liquid flow due to the forces connected with gradients of local surface tension. The appearance of such gradients becomes possible if the coefficient of surface tension depends on the concentration of the transferred substance. The interfacial turbulence arising from the interaction of mass fluxes and chemical reactions at free surface are increasingly attracting a great deal of interest for the study of reaction macrokinetics in liquid-liquid and gas-liquid systems. The concurrent effects due to diffusion-controlled transport of reactants on the one hand and to the concentration-dependent surface tension on the other hand can initiate the development unordered velocity and concentration field patterns.

The surface reaction alter the mass balance at the interface, thereby causing the change in effective surface tension. These reactions can affect markedly the conditions for the occurrence of interfacial turbulence and exert influence on the resultant turbulent motion characteristics.

The linear analysis performed earlier enabled us to define critical conditions for instability in the form of the dependence of Marangoni number on the rate of heterogeneous reaction and other physico-chemical parameters. The Marangoni number is the ratio of the work made by forces of local surface-tension gradient to the energy dissipation due to viscosity and diffusion.

For the case when the Marangoni number only slightly overcomes the critical value, a qualitative physico-chemical model is proposed which explains the mechanism of the flow generation on the basis of energy balance in the liquid layer in the presence of forces of local surface-tension gradient. Characteristic rates and the scale of flows were evaluated with the use of this model. Similar results were obtained more rigorously using non-linear theory of stability.

If the Marangoni number is much higher than the critical value, the regime of interfacial turbulence is realized in the system. It became possible to describe fields of average energy of turbulent fluctuations and average concentration in the liquid bulk with two-parametric model of turbulence. The possibility to close the set of equations of this model was analysed using qualitative physico-chemical assumptions on the dependence of average work of surface forces on the average consumption of surfactant in the heterogeneous chemical reaction.

Let us consider mass transfer from a liquid element moving along interface on the scale of a single fluctuation. The concentration of the surfactant in the element decreases due to heterogeneous chemical reaction. In its turn, this decrease in concentration controls local longitudinal gradient of surface tension which facilitates the increase in the velocity of liquid and, consequently, the increase in turbulent energy and local mass flow to the interface. Because these both factors are of the same physical nature and manifest themselves in the same scale of turbulent fluctuations, a correlation exists between the average work done by forces arisen due to the surface tension gradients and the average rate of consumption of the substance. Thus, the relation between averaged parameters of two-parametric model of turbulence in the presence of surface dynamic factors can be established only taking account of physico-chemical processes occurring on the scale of a single fluctuations.

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## 799.G4

MECHANICS BEHAVIOR ANALYSIS OF SOLIDIFIED  
COLLOIDAL MATERIAL

Wang Jianping

*Department of Engineering Mechanics, Wuhan University of Technology, Wuhan, P. R. China*

Solidified colloidal material has been widely applied to various fields. Because material possesses two special characteristics: nonhomogeneous and variable physical parameters, it is difficult for mechanics behavior to be described and accordingly the material's excellent function cannot be taken into

full play, which will result in the waste of material. Under this premise of conforming to each basic principle, this article gives the basic relation pattern that describes mechanics behavior of solidified colloidal material possessing nonhomogeneous and variable physical parameters.

## 800.G4 PHYSICAL CHEMISTRY AND PHYSICO-CHEMICAL MECHANICS OF POROUS POLYVINYLFORMALS

Zinoviev V.V.

*Institute of Physical Chemistry of the Russian Academy of Sciences, Moscow  
Scientific Research and Production Centre of the Structured Materials, Vladimir, Russia*

According to P.A. Rebinder the most important problem of colloid chemistry and physico-chemical mechanics is the creation of new materials having determined properties - the preparation of disperse structures using chemical reactions, dispergation processes and separation of new disperse phases.

The elaboration of the porous polyvinylformal (PVF), possessing of high waterholding capacity, shows as the most effectively the combination of the all this methodes.

The investigations of kinetics of interaction of the polyvinylalcohol (PVA) and  $\text{CH}_2\text{O}$  in strong acid aqueous solutions shows, that the fundamental reaction of pair wise substitution of neighbouring OH-groups creating the acetal rings is accompanied by rising of lonely OH-groups and reducing the rate of the reaction nearly the degree of substitution  $1-e^{-2}=0.8647$  (P.Flory-effect) by diffusion restraining in concentrated solutions of polymers, by rising of the intermolecular acetal bridges, by the growth of molecular masses and of the viscosity of the solution and by the formation of polymer space network.

During the acetalizing process the solubility of the polymer reduces, the stables solutions converts to the metastable, new disperse phase separates and condensation structures (cellulare or globular-reticulare) formates. After eliminating of reagents they transforms to the porous materials of the high waterholding capacity.

The condensation structures of PVF of low degree of substitution are capable by drying (by action of the forces of the capillary contraction or of the external pressure) to transform to the cryptoheterogeneous state, when the porosity disappears, the particles of the polymer phase fast glues one to another, but the formed quasihomogeneous; material saves the memory on his heterogeneous origin as a system of internal stresses. After swelling in water the cryptoheterogeneous PVF fully restores their initial porous structure. But when the internal stresses relaxes (e.g. by beating), this ability fully losses, PVF transforms to the common homogeneous polymer.

The using of the cryptoheterogeneous PVF is prevented by small rate of diffusion and of restoration of porosity. The processes goes sufficiently fast only in thin films. For fast swelling such material needs a complementary system of relatively broad transport pores, that creates by dispergation in the initial solution for synthese of PVF of sufficient amounts of gas (air), fluids (polyethyleneglycols) or solids (starch). The biggest transport pores may be obtained by beating of air into the fluid by mixers (for better stability of the foam a cationic surfactant added), the smallest one by dispergation of starch corns (with following elimination by hydrolisys).

Through regulation of disperse phase/dispersion medium relation, varying the molecular masses of PVA and its concentration in the initial solutions it is possible to obtain the porous PVF possessing the detemined complex of properties. The waterholding capacity of poroplasts, prepared by foaming, may be determined with precision  $\pm 10\%$ , prepared by use of starch dispersion-with precision  $\pm 5\%$ . The waterholding capacity usually vary from 10 to 30g/g, but may be rayseed to 50g/g.

Through their unique properties the porous PVF are used in the broad fields of technicsand medicine.

**801.H1****ORIENTATION OF LONG WAVELENGTH PIGMENTS  
IN PHOTOSYSTEM I PARTICLES****Atanaska Andreeva<sup>1</sup> and Maya Velitchkova<sup>2</sup>**<sup>1</sup>*Sofia University, Faculty of Physics, Department of Condensed Matter of Physics,  
5, J. Bourchier blvd., BG - 1164 Sofia, Bulgaria;*<sup>2</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, Acad. G. Bonchev str. bl. 21, 1113 Sofia, Bulgaria*

The fluorescence anisotropy of photosystem I particles, isolated from spinach chloroplasts and containing approximately 200 chlorophyll molecules per reaction center, has been investigated at low temperatures. The particles were oriented by uniaxial squeezing of polyacrylamid gels. Fluorescence anisotropy has been measured upon excitation with laser lines at 476.5 nm and 632.8 nm. The orientation of the long wavelength pigments - chlorophyll a molecules, that absorb at wavelengths longer than the corresponding reaction center, has been determined at 77K. Two pools of such pigments are found in green plants, named F720 and F735 according to their fluorescence maxima in nm. Our experimental results show that these spectral forms - F720 and F735 have a non-parallel emission dipoles. Using the new "practical" formula for the degree of polarization of a triple-chromophore complex under steady-state excitation, derived recently by Demidov, and our data for the fluorescence anisotropy at these temperatures, we calculate the rate of energy transfer between long wavelength pigments. The obtained results are compared to the previously reported values and are discussed in the frame of the Forster's mechanism of dipole-dipole energy transfer between long wavelength pigments.

This work was supported by the Foundation for Scientific Research at Sofia University, Bulgaria (project N°265).

**802.H1****FORMING OF STABLE CUPOLA-SHAPED BILAYER MEMBRANES  
WITH MOBILE PLATEAU-GIBBS BORDER****V.F. Antonov, E.V. Shevchenko, N.E. Bogatireva, E.Yu. Smirnova***Moscow Medical Academy, Menzhinskogo 9, Moscow 129327, Russia*

The planar lipid bilayer membranes (BLAO) have been widely used for study of the permeability of biological membranes. But the shape of cell membranes not planar, but close to spherical. Cupola-shaped bilayer lipid membranes have been formed under a hydrostatic pressure gradient. The electrolyte evaporation in one compartment of camera was reason of this gradient. The stability of cupola-shaped membrane implies an equilibration of hydrostatic pressure by Laplace pressure.

$$\rho \cdot g \cdot \Delta h = 4\sigma/R \quad (1)$$

At first the hydrostatic pressure was a reason of shape changing of membrane from plane to the surface of spherical segment. The increasing of pressure produced the radius decreasing. It was continued until the shape of membrane became hemispherical with radius equal to hole radius. After this moment the evaporation was continuing, the volume of membrane segment was increasing too, but a hydrostatic pressure was decreasing (in accordance with formula 1). If the surface of Teflon wall was processed with lipid solution the Plateau-Gibbs border could move from the hole. The radius of membrane is increasing with time and it is connected with the evaporation speed.

We calculated the dependency between evaporation volume and radius of membrane. We compared the theoretical calculations with results of experiments. In experiments we studied the capacitance change. All experiments were performed with hydrogenated egg lecithin. The capacitance of membrane was depended on area and thickness. The change was connected with area change, but thickness change because capacitance of planar membrane in the beginning of experiment was equal to bilayer lipid membrane (0.3  $\mu\text{f}/\text{cm}$ ) and the thinning of such membrane was impossible. We studied the changes in lipid bilayer area at the phase transition of lipid. The temperature of phase transition of HEL is 51 °C. The membrane was formed at the temperature about 60 °C and then temperature was decreasing to 40 °C with constant speed 1°C/min, then membrane was heated with high velocity (about 40 °C/min). The main results are shown in fig. 1. It is shown that cooling of BLM from 60 °C to 50 °C has been followed by an initial increase of capacitance with reaches a peak near 50 °C and is accomplish by a drop of capacitance at much lower temperature than the phase transition temperature. The spontaneous drop of capacitance reflects the

shrinkage of membrane which occurs in gel-state. We suppose that a reasonable explanation of this effect is the change of surface tension. The surface tension in liquied-crystalline state is  $10^{-3}$  N/m, in gel-state is  $5.10^{-3}$  N/m. The dependence between evaporation volume and area of membrane for gel-state is shown on fig.2. At the temperature of phase transition the surface tension change produce radius drop.

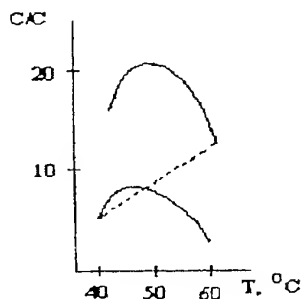


fig.1

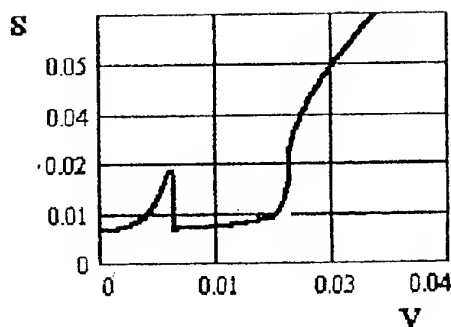


fig.2

### 803.H1 SYNTHETIC PHYTANYL-CHAINED GLYCOLIPID MEMBRANES: MEMBRANE PROPERTIES AND FUNCTIONAL INCORPORATION OF PHOTOSYNTHETIC PROTEIN COMPLEXES

Teruhiko Baba<sup>1</sup>, Hiroyuki Minamikawa<sup>1</sup>, Masakatsu Hato<sup>1</sup>, Akihiro Motoki<sup>2</sup>, Masahiko Hirano<sup>2</sup>

<sup>1</sup>National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

<sup>2</sup>Toray Research Center, Inc., 1111 Tebiro, Kamakura 248, Japan

Archaeobacteria inhabit under extreme conditions such as very high temperature, low pH or very high salt concentration, therefore, their membranes are considered to be chemically and physically stable. Using these unique membrane properties for construction of lipid-membrane protein assemblies, it is expected that the very stable sub-micron scale reactors can be developed. In this paper, we present the newly synthesized phytanyl-chained glycolipids as model lipids of archaeobacteria and their membrane properties. Further, the applicability of these membranes to the protein reconstitution was also examined. Photosystem II complexes (PS II) of thylakoid membrane from the thermophilic cyanobacterium *Synechococcus elongatus* were chosen as target membrane proteins for this purpose because the glycolipids contained in thylakoid membranes are thought to play important roles in the intra-membrane lipid-protein association state and the modulation of the protein functions. 1,3-bisphytyl glyceryl ether glycolipids, Glc(Phyt)<sub>2</sub> and Mal<sub>N</sub>(Phyt)<sub>2</sub> ( $N=2-5$ ) were synthesized (Fig.1). The glycolipids bearing the longer hydrophilic chain ( $N>3$ ) formed the lamellar liquid-crystalline ( $L_{\alpha}$  phase) in water, and also formed flexible lipid assemblies such as myelin figures and vesicles, whose permeabilities (*e.g.*, against  $\text{CO}_2^{2+}$ ,  $\text{H}^+$ ) were significantly lower than those formed with a natural glycolipid (DGDG) or phospholipids (*e.g.*, DPPC). They showed no obvious phase transition in the range of  $-120^{\circ}\text{C}$  to room temperature. On the contrary, Glc(Phyt)<sub>2</sub> and Mal<sub>2</sub>(Phyt)<sub>2</sub> formed the non-lamellar structures (*e.g.*, reverse hexagonal liquid-crystalline,  $H_{II}$  phase) in water. Surfactant-solubilized PS II was incubated with vesicle membranes prepared from mixtures of lamellar-forming lipid, non-lamellar forming lipid and an anionic sulfolipid (SQDG) to incorporate PS II into vesicles. In the absence of vesicles, the oxygen evolution activity of PS II was almost lost after incubation at  $40^{\circ}\text{C}$  for 1 hr. In the presence of vesicles, however, the activity was maintained depending on the kind of lipids and lipid/protein ratio. The amount of PS II incorporated into vesicles was estimated by ultracentrifugation. Judging from these results, the PS II in membrane was considered to retain its original activity. The effect of the lipid composition of vesicles on the PSII activity will be also presented.

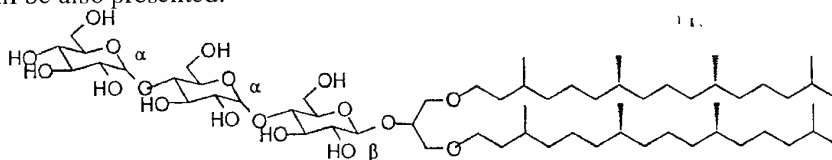


Fig.1 Chemical structure of Mal<sub>3</sub>(Phyt)<sub>2</sub>



## 804.H1 MODIFICATION OF POPE MODEL MEMBRANES BY SURFACTANT

N. Baboi<sup>1</sup>, G. Rapp<sup>3</sup> and S. S. Funari<sup>2</sup>

<sup>1</sup>Inst. Atomic Physics, Electron Accelerator Laboratory, POB MG 36, Bucharest, Romania

<sup>2</sup>MPIWI-Colloids and Surfaces, Teltow, Germany

<sup>3</sup>EMBL-Outstation Hamburg, Notkestraße 85, D-22603 Hamburg, Germany

Phospholipid/water systems form bilayer structures which constitute the simplest equivalent to biological membranes. Additives can induce changes in this morphology, leading to different structures.

Aqueous 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphatidylethanolamine (POPE) shows a gel phase at low temperatures which changes into a lamellar  $L_\alpha$  phase above 41°C and then into an inverted hexagonal phase [1]. Di-ethylene-oxide-mono-dodecyl-ether ( $C_{12}EO_2$ ) and water at concentrations <80 wt% forms a lamellar  $L_\alpha$  phase below 20°C. Heating it leads to an intermediate bicontinuous cubic phase in the concentration range between 30 and 70 wt% [2].

We investigated the ternary system POPE/ $C_{12}EO_2$ /water using small and wide angle X-ray diffraction (SAXS and WAXS), and polarising optical microscopy (POM). The phases and the corresponding transition temperatures between them were determined.

Samples with different compositions were transferred into capillaries and than flame sealed. The measurements were performed at the beam line X13 (EMBL - Hamburg) using a wavelength of 0.15 nm and heating/cooling rates of 2°C/min. Diffraction patterns were accumulated for 5 sec with 2 of them recorded per minute.

A sample containing POPE (36.0),  $C_{12}EO_2$  (57.6) and  $H_2O$  (6.4) wt% showed a  $L_\beta$  to  $L_\alpha$  phase transition at 32°C, a large decrease compared to the same transition inaqueous POPE, at 41°C, Fig.1. This is strong evidence that the head group interactions determine the structural behaviour of the system. The surfactant molecules disperse the lipid ones, weakening the lipid-lipid interactions and consequently decreasing the stability of the gelphase.

Moreover, below room temperatures non-lamellar phases were observed. These structures contain high curvature at the head group region. Normally they form inverted type structures which means a stronger interaction of the head groups than in the lamellar phases. Detailed analysis of the diffraction patterns are in progress and will be discussed. The phase diagram of this system shall be compared with POPC/ $C_{12}EO_2$ /water [3], evidencing the influence of a different head group.

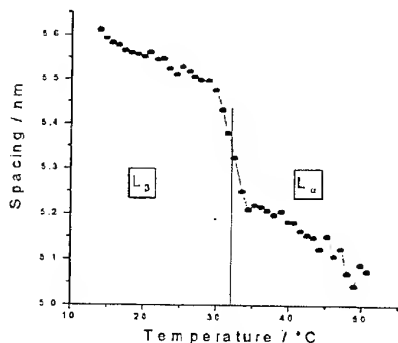


Fig. 1. Variation of the intralamellae repeat distance with temperature on a heating scan. The temperature of the phase transition is marked by a line. It parallels the vanishing of WAXS reflexions, characteristic of the gel phase.

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## 805.H1

### GENERAL EQUATIONS OF A HETEROPHASE EQUILIBRIUM OF A BIOMEMBRANE

A. A. Boulbitch

Fakultät für Physik, TU München, Physik-Dept. E-22, D - 85748 Garching bei München, Germany

Real biomembranes consist of multicomponent lipid alloys and contain various dissolved non-lipid molecules. Integral and anchored proteins also can be considered as those dissolved in a bilayer. Phase transitions accompanied by phase separations affect many membrane properties, such as transport, enzyme functions, drug susceptibility and interaction with anaesthetics, giving rise to an interest to the phase transition phenomena in lipid bilayers. Conventionally one can consider two limiting cases of phase transitions: weak or strong ones. In the limiting case of strong transition one can consider the state of a

membrane to be almost invariable along its surface up to the phase boundaries. In this case the state equations are reduced to algebraic ones and do not describe the phase boundary itself. The latter is narrow and its equilibrium should be determined by special conditions. A curved bilayer membrane divided into two regions containing different phases is considered. The phases are separated by a narrow phase boundary. The equations of equilibrium of this system describing the bulk states of phases, the membrane shape and the conditions on the phase boundary are obtained in the most general case.

## 806.H1

### SURFACE FORCES IN BIOLOGICAL MEMBRANES

**L.R. Fisher**

*Department of Physics, University of Bristol, Tyndall Avenue, Bristol BS8 1TL, United Kingdom*

The author has developed a technique for handling and measuring the forces between deformable particles. The key to the technique is the use of a flexible micropipette, mounted on a micromanipulator, to handle the particle of interest. The particle is held at the tip by suction, and may be introduced to a surface of interest or to a second particle (held by a second micropipette). After contact, the flexible micropipette is used to apply a detachment force. The applied force is calculated from the bending of the pipette, while the topology of contact is monitored by videomicroscopy. Forces as low as a picoNewton (less than that required to break a hydrogen bond) may be measured.

The technique has been applied to a wide range of situations of interest to colloid scientists. Attention here will be focussed on its use in measuring the forces between red blood cells and defined substrates. The adhesion of red blood cells to hydrophilic and hydrophobic substrates will be discussed, together with recent work on the use of the technique to measure the effects of the cell surface environment on the strength of adhesive ligand/receptor interactions.

## 807.H1

### MECHANISMS UNDERLYING THE DESORPTION OF LONG CHAIN LIPIDS BY CYCLODEXTRINS

**Margarita Ivanova<sup>1,2</sup>, Robert Verger<sup>2</sup> and Ivan Panaiotov<sup>1</sup>**

<sup>1</sup>*Biophysical Chemistry Laboratory, University of Sofia, Bulgaria*

<sup>2</sup>*UPR 9025 du CNRS, Laboratoire de Lipolyse Enzymatique, Marseille, France*

The desorption rates of monolayers of insoluble lipids, oleic acid and monoolein, spread at the air/water interface were measured in the presence of  $\beta$ -cyclodextrin or  $\alpha$ -cyclodextrin at various subphase pH values. The desorption rates of the CD/OA inclusion complex at pH 2 can be satisfactorily described by a kinetic Langmuir equation revealing the existence of an energy barrier in the complex formation of the CD/OA. The dramatic increase observed in the desorption rates of the CD/OA complex at alkaline pH is in agreement with the theoretical prediction that a diffusion process is likely to occur from the surface to the bulk phase. Our results are consistent with the formation of hydrogen bonds between the ionized OA monolayer at pH 11 and the O(6)H groups in the CD cavity.

## 808.H1

### INVESTIGATION OF THE CYCLODEXTRIN-SOYBEAN OIL INCLUSION COMPLEXES AT THE OIL/WATER AND AIR/WATER INTERFACE

**M. Ivanova<sup>1,2</sup>, S. Labourdenne<sup>2,3</sup>, A. Cagna<sup>3</sup>, F. Boury<sup>4</sup>, R. Verger<sup>2</sup> and I. Panaiotov<sup>2</sup>**

<sup>1</sup>*Biophysical Chemistry Laboratory, University of Sofia, Bulgaria*

<sup>2</sup>*UPR 9025 du CNRS, Laboratoire de Lipolyse Enzymatique, Marseille, France*

<sup>3</sup>*ITConcept, Longessaigne, France*

<sup>4</sup>*Pharmacie Galénique et Biophysique Pharmaceutique, Faculté de Pharmacie, Angers, France*

The  $\alpha$  and/ or  $\beta$ -cyclodextrin-soybean oil inclusion complexes were investigated at the oil/water interface using the dynamic drop method and a new rheological approach. The results were compared with those obtained at the air/water interface. The organisation of the inclusion complexes at the two interfaces were discussed.

## 809.H1 THERMOTROPIC AND BAROTROPIC PHASE TRANSITION ON BILAYER MEMBRANES OF PHOSPHOLIPIDS WITH VARYING ACYL CHAIN-LENGTHS

Shoji Kaneshina<sup>1</sup>, Hayato Ichimori<sup>2</sup>, Takashi Hata<sup>1</sup>, Shoji Maruyama<sup>1</sup>, and Hitoshi Matsuki<sup>1</sup>

<sup>1</sup>*Department of Biological Science and Technology, Faculty of Engineering,*

*The University of Tokushima, Minamijosanjima, Tokushima 770, Japan*

<sup>2</sup>*Anan National College of Technology, Anan, Tokushima 774, Japan*

The bilayer phase-transition of a series of 1,2-diacylphosphatidylcholines containing linear saturated acyl chains of even- and odd- number carbons ( $C = 12, 13, 14, 15, 16, 17$ , and  $18$ ) were observed by two kinds of optical methods. One is the observation of isothermal barotropic phase transition and the other is the isobaric thermotropic phase transition. The temperature of the main transition from the gel ( $P_\beta'$ ) phase to the liquid crystalline ( $L_\alpha$ ) phase for each lipid was elevated linearly by pressure in the range of  $150$  MPa. The slope of the temperature-pressure diagram,  $dT/dp$ , was almost constant in the range of  $0.19 - 0.22$  K MPa<sup>-1</sup>. The chain length dependence of the main transition temperature under ambient pressure described a smooth curve with no evidence of odd/even discontinuities. The phase transition enthalpy,  $\Delta H$ , was determined by the differential scanning calorimetry. The value of  $\Delta H$  increased with an increase in the acyl chain-length. The  $\Delta H$  vs. chain-length curve was non-linear and convex upward. The volume change,  $\Delta V$ , associated with the transition was calculated from the values of  $\Delta H$  and  $dT/dp$  by means of the Clapeyron-Clausius equation. The values of  $\Delta V$  increased with an increase in the acyl chain-length. The contribution of acyl-chain to the volume increment for the transition amounts to  $1.2 - 2.1$  cm<sup>3</sup> mol<sup>-1</sup> per one methylene group.

## 810.H1 THE DEPENDENCE OF PROPERTIES OF SYRINGOMYCINE INDUCED ION CHANNELS ON THE SCREENING EFFECT OF MEMBRANE SURFACE CHARGE

Yu.A.Kaulin<sup>1</sup>, L.V.Schagina<sup>1</sup>, A.M.Feigin<sup>2</sup>, M.P.Sidorova<sup>3</sup>, J.Y.Takemoto<sup>4</sup>, J.H.Teeter<sup>2,5</sup>, J.G.Brand<sup>2,5</sup>

<sup>1</sup>*Institute of Cytology of RAS, St. Petersburg, Russia*

<sup>2</sup>*Monell Chemical Senses Center, Philadelphia, USA*

<sup>3</sup>*St. Petersburg State University, Dept. Chem., St. Petersburg, Russia*

<sup>4</sup>*Utah State University, Logan, USA*

<sup>5</sup>*University of Pennsylvania, Philadelphia, PA, USA*

The antifungal cyclic lipodepsipeptide, syringomycin-E (SRE), induces voltage-gated ion channels of weak anion selectivity in planar lipid bilayers (Feigin et al., J. Membr. Biol. 149, 41-47, 1996). Here we present data showing that properties of these channels, formed in the bilayers of an equimolar mixture of 1,2-dioleoyl-sn-glycero-3-phosphoserine (DOPS) and 1,2-dioleoyl-sn-glycero-3-phosphoethanolamine (DOPE), depend on the electrolyte concentration of the bathing solution. The screening of the surface charge of the membrane by ions of the electrolyte leads to changes of voltage dependence of the gating properties of the channels. The single channel conductance increased, and the anion selectivity decreased with increasing electrolyte (NaCl) concentration. The anion transference numbers for SRE-treated membranes decreased from  $0.83$  to  $0.70$  when NaCl concentration in the membrane bathing solution increased from  $0.01$  to  $1$  mol/l respectively. Two types of channels were observed at different concentrations of NaCl: "small" and "large" ones. The ratio of conductance of large to small channels was approximately equal to  $6$ . This value did not depend strongly on the concentration of NaCl in the bathing solution nor on the voltage applied to the membrane. However increasing NaCl concentration from  $0.01$  to  $1$  mol/l decreased the probability of the appearance of large channels and increased the probability of the appearance of small channels. The mechanisms by which the selectivity and probabilities of the appearance of small and large channels depend on salt concentration are discussed.

## 811.H1

MIXING BEHAVIOR OF SATURATED SHORT-CHAIN  
PHOSPHATIDYLCHOLINES AND FATTY ACIDSRumiana Koynova<sup>1</sup>, Boris Tenchov<sup>1</sup> and Gert Rapp<sup>2</sup><sup>1</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*<sup>2</sup>*EMBL - Outstation Hamburg, D-22603 Hamburg, Germany*

Temperature-composition phase diagrams of the hydrated pseudo-binary mixtures dilauroylphosphatidylcholine (DLPC) / lauric acid (LA) and dimyristoilphosphatidylcholine (DMPC)/myristic acid (MA) have been constructed using high-sensitivity DSC and time-resolved X-ray diffraction. They are of different type compared to those of the longer chain phosphatidylcholine/fatty acid mixtures, the latter being of maximum azeotropic point type. Eutectic points were distinguished in the phase diagrams of both DLPC/LA and DMPC/MA mixtures, at 75 mol% MA and 49 °C for the DMPC/MA mixture, and at ca. 67 mol% LA and 29 °C for the DLPC/LA mixture. Compositional regions of phase separation have been located according to the shape of the phase diagrams and observed by X-ray diffraction. Thus, between ca. 60 and ca. 90 mol% fatty acid (FA), solid phase immiscibility is detected. Also, limited regions (2-4 °C) of liquid - liquid phase immiscibility exist at compositions with slightly prevailing fatty acid molar content. Thus, at 67 mol% MA, a phase separation between  $L_{\alpha}$  phase enriched in DMPC and  $H_{II}$  phase enriched in MA takes place in the temperature range 51 - 55 °C. With the eutectic composition (75 mol% MA), a direct melting into the  $H_{II}$  phase is observed. The studied PC / FA mixtures form compound subgel polymorphic phases (one in the DMPC/MA mixture and two in the DLPC/LA mixture) upon low-temperature equilibration. In the liquid crystalline phase region, non-lamellar phases dominate the phase diagrams, especially in their fatty acid-rich part. With increasing FA content, they arrange in the sequence: bicontinuous cubic phases ( $Ia3d$ ,  $Pn3m$ ,  $Im3m$ )  $\rightarrow$  hexagonal phase ( $H_{II}$ )  $\rightarrow$  micellar cubic phase ( $Fd3m$ )  $\rightarrow$  isotropic phase (I). At a given lipid composition, the order of appearance of the cubic phases with increasing temperature varies with the sample composition. They exist either as single phases or concurrently to the hexagonal  $H_{II}$  phase.

## 812.H1

AUTOMATIC OIL-DROP TENSIO METER FOR INVESTIGATING  
THE ACTIVITY OF LIPOLYTIC ENZYMESS. Labourdenne<sup>1,2</sup>, M.G. Ivanova<sup>1,3</sup>, C. Riviere<sup>1</sup>, A. Cagna<sup>2</sup>, B. Delorme<sup>2</sup>, G. Esposito<sup>2</sup>, R. Verger<sup>1</sup><sup>1</sup>*Laboratoire de lipolyse enzymatique, UPR 9025 de l'IFRC1 Biologie structurale et microbiologie, CNRS, 31 chemin Joseph Aiguier 13402 Marseille Cédex 20, France*<sup>2</sup>*IT Concept, parc de Chancolan 69770 Longessaigne, France*<sup>3</sup>*Biophysical Chemistry University of Sofia, James Bourchier 1, 1126 Sofia, Bulgaria*

An automatic digitized oil-drop tensiometer was developed and used to investigate the activity of lipolytic enzymes on long chain triacylglycerols at an oil/water interface. Enzymatic reactions of this kind can be monitored either by recording the variations with time in the interfacial tension resulting from the accumulation of lipolytic products at the interface or by keeping the interfacial tension at a fixed-end point value by increasing the area of the oil drop. It was established that the initial decrease of the interfacial tension was strictly proportional to the lipase concentration present in the glass cuvette. To elucidate the elementary stages involved in enzymatic lipolysis at the oil/water interface, we studied the surface behaviour of the lipolytic products, using the monomolecular film technique in the absence of any enzyme. The oil-drop tensiometer was then used to study the action of the Human Pancreatic Lipase (HPL) and the effects of colipase and bile salts on the hydrolysis of the oil drop by this human pancreatic lipase (HPL). Biotin labelled HPL (HPL\*) was used in an ELISA test to determine the amount of HPL\* adsorbed at the drop surface, which was responsible for the changes in the interfacial tension. Less than 1 % of the total amount of HPL\* injected into the glass cuvette was found to be adsorbed at the oil-water interface. At bile salts concentrations below their critical micellar concentration (CMC), these detergents had no effect on either the binding of HPL\* or the rate of hydrolysis. In addition, colipase does not increase the adsorption of HPL\* but considerably enhances the turn over of HPL at the oil/water interface. Colipase can therefore be said to behave like a true cofactor of HPL. The Michaelis-Menten model adapted for dealing with catalysis in heterogeneous media was used to compare the lipase-colipase effect on monomolecular films at air/water and oil/water interfaces. The oil-drop tensiometer can also be used to study the kinetics of phospholipase  $A_2$  at the oil/water interface.

## 813.H1 ION PERMEABILITY OF A MEMBRANE WITH SOFTPOLAR INTERFACES

Victor Levadny<sup>1,3</sup>, Vicente Aguilera<sup>1</sup>, and Marina Belaya<sup>1,2</sup>

<sup>1</sup>Universidad Jaume I, 12080 Castellon, Spain

Permanent Adresses: <sup>2</sup>Institute of Plant Physiology, Russian Acad. of Sci., Moscow, Russia

<sup>3</sup>The Scientific Council for Cybernetics, Russian Acad. of Sci., Moscow, Russia

We have analysed the ion transport across a membrane with extended soft permeable interfaces (polar zones), placed in an aqueous solution, under short-circuit conditions. We have taken into account the existence of fixed charges and dipoles in these membrane interfaces. The membrane has been modelled as composed of three layers: an inner hydrophobic layer and two polar zones. Nernst-Planck's equation has been used for describing the ion transport and Goldman's approximation has been assumed to be valid for the hydrophobic layer. In the present study we have considered three limit cases, i) the inner hydrophobic layer as the rate determining step; ii) the polar zones as the rate determining step; iii) the dipoles interface as the rate determining step. Mathematical criteria for them has been obtained. The main transport characteristics of the considered system (permeability, permselectivity, etc.) have turned out to be essentially different in each case. The influence of the electrolyte concentration, the surface dipole density and thickness of the polar zone on the total ion flux and permselectivity has been analysed. It has been shown that the permselectivity of such system depends significantly on all these parameters. Particularly, the permselectivity of the same membrane changes with bulk electrolyte concentration. A general expression for cation selectivity has been obtained. The connection of the developed theory with experimental results has been discussed.

## 814.H1 SOLID STATE <sup>2</sup>H and <sup>31</sup>P NMR IN WATER-LIPID SYSTEMS

R. Marinov<sup>1</sup>, E.J. Dufourc<sup>2</sup> and A. Derzhanski<sup>1</sup>

<sup>1</sup>Institute of Solid State Physics, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria,

<sup>2</sup>Centre de Recherche Paul Pascal, CNRS, 33600 Pessac, France

The phase behaviour and water dynamics of model water-lipid systems were studied by means of solid state deuterium (<sup>2</sup>H) and phosphorus (<sup>31</sup>P) NMR. The influence of cholesterol on the phase transition temperatures was observed. Model of lyotropic liquid crystal phase transitions was proposed.

The solid state <sup>2</sup>H and <sup>31</sup>P NMR are powerful methods for investigation of the water dynamics and lipid polymorphism in water-lipid systems. By using these techniques we studied the phase behaviour of the system palmitoyl-oleoyl-phosphoethanolamine - water with and without addition of 30 mole cholesterol<sup>1,2</sup>. The phase diagrams were obtained in the water concentration region 3+300 mole water/mole lipid and temperatures from 278K to 360K. In these conditions three phases were observed - lamellar gel, lamellar liquid crystal and inverted hexagonal one.

The addition of cholesterol suppressed the lamellar gel to lamellar liquid crystal phase transition and decreased the lamellar-to-inverted hexagonal phase transition temperature with about 20K. To describe this behaviour we proposed a model of the lyotropic liquid crystal phase transitions<sup>3</sup>. Our model is based on the calculation of the deformation energy, necessary to change the real molecular shape in order to satisfy the geometrical requirements of packing in the different phases. The calculated phase transition temperatures are in good agreement with the experimental results.

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## 815.H1 SUPPORTED AND SELF-ASSEMBLED BILAYER LIPID MEMBRANES AS AN ADAPTIVE MATERIAL FOR BIOTECHNOLOGY

A. Ottova<sup>1,2</sup>, T.-A. Zhou<sup>1</sup>, V. Tvarozek<sup>2</sup>, Huipin Yuan<sup>3</sup>, Xiandao Lu<sup>4</sup>, and H.Ti Tien<sup>1</sup>

<sup>1</sup>Department of Physiology, Michigan State University, East Lansing, MI 48824, USA

<sup>2</sup>Center for Interface Sciences, Microelectronics Department, Slovak Technical University, Bratislava, SR

<sup>3</sup>Analytical and Testing Center of Sichuan Union University, Chengdu, PRC

<sup>4</sup>School of Pharmaceutical Science, Beijing Medical University, Beijing 100083, PRC

There have been a number of reports recently on self-assembled molecules or structures as "adaptive materials" or "smart materials" [1]. Without question, the inspiration for this exciting work comes from the biological world, where the lipid bilayer of cell membranes plays a pivotal role in signal transduction and information processing. This is owing to the fact that most physiological activities involve some kind of lipid bilayer-based receptor-ligand contact interactions. There are many outstanding examples such as ion sensing, antigen-antibody binding, and ligand-gated channels, to name a few. Our approach to study these interactions in vitro is facilitated by using self-assembled bilayer lipid membranes (s-BLMs). Self-assembled bilayer lipid membranes on solid supports (s-BLMs) and gel supports (sb-BLMs) may be formed by a number of methods [2]. Recently, we have found that s-BLMs doped with fullerenes (e.g., C60) can function as sensors and generate photoelectric effects. These new s-BLMs have been characterized by cyclic voltammetry [3]. We have focused the efforts on ion and/or molecular selectivity and specificity using supported BLMs, whose enhanced stability greatly aids in research areas of membrane biochemistry, biophysics and cell biology as well as in biosensor designs and molecular devices development [4]. In this paper, our current work along with the experiments carried out in close collaboration with others on s-BLMs will be presented [5,6,7].

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## 816.H1 POLYVINYL CHLORIDE MEMBRANE IN IMMUNOSENSOR DESIGN

Panasyuk T., Piletsky S., Nigmatullin R., El'skaya A.

*Institute of Molecular Biology and Genetic, National Academy of Sciences (Ukraine)*

A considerable number of different polymer materials have been investigated in view of their application in bioaffinity and biomimetic sensors. Their use in such devices serves to enhance the stability, biocompatibility, and selectivity.

In this communication we present the application of such materials in immunosensor as support for antibody and in the same time as active part of the transducer. The sensor is based on bioaffinity polymeric membrane (with immobilized Ab) able to change its ions permeability during immunochemical reaction. Such membranes are responsible for both molecular recognition and signal generation. In our experiments we used non-charged polyvinyl chloride membranes for Ab immobilization. The ion permeability was analyzed in electrochemical cell with platinum electrodes separated by the membrane under investigation. Measurement of the sensor response was performed by applying a small-amplitude alternating voltage to the electrodes. The electrical conductivity of the system with the Ab-bound membrane increases in the presence of Ag allowing to detect its concentration. The sufficient sensitivity (5 ng/ml) and higher rate as compared with ELISA-method (the response time is 5-6 min) were achieved.

Membrane potential measurements of the PVC films allow to explain possible mechanism of signal generation. The membranes proposed can be used for express detection of different analysis in medicine, biotechnology and environmental pollution monitoring.

## 817.H1 SHORT-RANGE ATTRACTIONS BETWEEN TWO COLLOIDS IN A LIQUID MONOLAYER

T. Sintes and A. Baumgärtner

*Forum Modellierung and Institut für Festkörperforschung, Forschungszentrum, 52425 Jülich, Germany*

Biological membranes are highly heterogeneous. Besides of lipids they contain various inhomogeneities such as proteins and cholesterol. Many of the proteins are mobile and aggregate into islands which are important for cellular activities.

Several mechanisms have been proposed to contribute to the process of aggregation. One mechanism is due to specific intermolecular forces [1] encountered for example at temperature driven phase separations among lipids and proteins [2]. Another situation is concerned with asymmetric properties of curved membranes and asymmetric shapes of embedded proteins which both may induce aggregation of proteins. A third class of aggregation mechanism is related to long-range membrane-mediated attraction between two inclusions [3-5]. The latter force is due to the correlation between the perturbations imposed by the inclusions on the membrane's long-range undulations. This mechanical coupling between the inclusions and the undulations of the membrane leads to a  $1/R^4$  type attraction [4].

This latter type of attraction may be limited to large distances where contributions of local fluctuations of the lipids are unimportant. At short distances, however, say in the order of the size of the lipids, entropic effects can be expected to play a significant role. This short-range interaction may be important for the stabilization of tight clusters of inclusions encountered, e.g., during the aggregation of pore forming membrane helices.

Our investigations demonstrate that a non-specific attraction between two inclusions exists and is of short-range. We will show that two mobile cylinders embedded in a lipid monolayer exhibit two types of short-range attractions, a depletion-induced attraction in the range  $r < \sigma_L$ , where  $\sigma_L$  is the diameter of a lipid and  $r$  is the distance between the surfaces of the two cylinders, and a fluctuation-induced attraction in the range  $1 < r/\sigma_L < 4$ . Using Monte Carlo methods we have calculated the force between the cylinders for various diameters  $\sigma_p$ . Evidence is given that the strength of attraction increases with decreasing curvature of the cylinders.

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## 818.H1 THEORETICAL AND EXPERIMENTAL STUDY OF THE GEOMETRY OF COEXISTING PHASES IN BILAYERS OF MIXED PHOSPHOLIPIDS

Vladimir Smorodin<sup>1,2</sup>, Eurico Melo<sup>1</sup>

<sup>1</sup>*ITQB-Instituto de Tecnologia Química e Biológica, Apartado 127, P-2780 Oeiras, Portugal*

<sup>2</sup>*Department of Chemistry, Moscow State University, Moscow 119899, Russia*

Phospholipid bilayers composed of lipid mixtures form non-ideal mixtures which exhibit phase separation in certain temperature, pH and ionic strength ranges, at constant pressure. It has been proposed that this membrane heterogeneity can be used by the cells to control its physiology by modulating the efficiency of reaction between membrane bound components (Melo *et al.*, 1992). The geometry and



topology of the two coexisting phases in this phase coexisting region have never been directly observed probably because at least one of the linear dimensions of the objects is submicroscopic. In Langmuir-Blodgett monolayers with the same composition, the phase-separation is visible with an optical fluorescence microscope and the rigid domains have a characteristic elliptical shape at the beginning, growing in spiral-like formations.

Fluorescence recovery after photobleaching (FRAP) is a well established technique for the study of the lateral diffusion coefficient in two dimensional samples. The study of molecular diffusion in the phase coexistence region of a bilayer using FRAP (Vaz *et al.*, 1989) allowed us to estimate the dimension of the rigid units clustering together to constitute the rigid phase network. To interpret this experimental data we modeled the rigid units as ellipses based on the observations in monolayers (Keller *et al.*, 1987). In result, we have found that for several phospholipid systems the FRAP curves could be simulated if ellipses have a long axis between 1-2  $\mu\text{m}$  and an aspect ratio of 0.2 to 0.3.

We also present a possible theoretical explanation for rigid domains in bilayer assemblies being much smaller than those observed in equivalent monolayers. In our theoretical considerations we neglected electrostatic interactions between separate solid domains, an assumption valid for small solid fractions. By evaluating the part of the Gibbs free energy of crystallisation due to the polarization density in both cases we were able to rationalize the smaller sizes of bilayer rigid domains observed in our experiments.

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## 819.H1 INTERACTION OF PHARMACEUTICAL PREPARATION WITH MODEL LIPID MEMBRANES

Syomina I.G., Faizullin D.A., Stupishina E.A.

*Kazan Institute of Biology of the Russian Academy of Sciences, Kazan, Russia*

Pharmaceutical preparation CAPAH (( 2 - chloroethoxy) (p-N,N-dimethylaminophenyl)phosphinyl-acetohydrazide) exerts stabilizing action on membranes of erythrocytes. For finding out the mechanism of this effect, interaction of CAPAH with artificial lipid membranes was studied. Dispersion lipid-water and single bilayer liposomes of phosphatidylcholine were used as model systems. Infrared spectroscopic observations reveal interaction of a preparation with molecules of phospholipid. In spectra of liposomes with addition of a preparation displacement of a band valent fluctuations of ether group C=O in low-frequency area is observed that testifies to formation of hydrogen bond. There were no changes of IR-spectrum in the area of fatty acidic tails. The influence of concentration of pharmaceutical preparation, temperature, introduction of cholesterol in liposomes composition on degree of CAPAH effect was studied. Obtained data agree well with ESR investigations. Study of interaction of biologically active substances with model membranes allows to make more detailed representation about molecular basis of pharmaceutical effect of a preparation on natural membranes.

## 820.H1 EFFECT OF PHOSPHOLIPASE D ON THE ELECTRIC DIPOLE MOMENTS AND CHARGE DISPLACEMENT OF PURPLE MEMBRANES

S.G. Taneva<sup>1</sup>, A. Dobrikova<sup>1</sup>, Tóth-Boconádi<sup>2</sup> and I. Petkanchin<sup>3</sup>

<sup>1</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*Institute of Biophysics, Biological Research Center, Hungarian Academy of Sciences,  
Szeged H-6701, Hungary*

<sup>3</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

The electric dipole moments of purple membrane (PM), photocycle were investigated in membrane fragments modified by phospholipase D (PLD). Purple membranes from *Halobacterium salinarum* have unusual lipid composition [1, 2]. The PM lipids are organized in a typical bilayer structure and asymmetrically distributed between the two membrane surfaces [3, 4]. It has been shown that PLD cleaves the major purple membrane lipid (in the form of liposomes and in PM) releasing dialkylglycerol and glycerol



biphosphate [5]. The effect of phospholipase D on the surface electrical properties (permanent dipole moment and electric polarizability) of PM deduced from Electric Light Scattering studies [6]. The kinetics of the charge displacement and  $M_{412}$  photointermediate the photocycle of bacteriorhodopsin (bR) were investigated. Data show that the modification of the head group of the major purple membrane phospho-lipid by phospholipase D affects the surface electric properties, the ms-transient absorbance kinetics of  $M_{412}$ , and reduces the proton pumping activity of bR.

The decrease of the values of the electric dipole moments and the reduction of the pumping activity induced by the enzymatic modification of PM lipids are similar to those observed upon partial delipidation of PM by the surfactants, CHAPS [7] and Tween 20 [8]. This proves a strong contribution of the membrane lipids and the lipid head groups to the electrical properties of purple membranes.

This work was partly supported by contract K-519 from Bulgarian National Fund, Science Research, by the Basque Government (fellowship PGV 9242) and by the Institute of Biophysics, Hungarian Academy of Sciences.

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## 821.H1 ACCELERATED FORMATION OF CUBIC PHASES IN LIPID DISPERSIONS

Boris Tenchov<sup>1</sup>, Rumiana Koynova<sup>1</sup> and Gert Rapp<sup>2</sup>

<sup>1</sup>*Institute of Biophysics, Bulg. Acad. Sci., 1113 Sofia, Bulgaria*

<sup>2</sup>*EMBL-Outstation Hamburg, Notkestrasse 85, D-22603 Hamburg, Germany*

The interest in the ability of the membrane lipids to form cubic and inverted hexagonal liquid crystalline phases stems out from the increasing evidence that the non-lamellar lipid patterns play important role in cellular processes such as cell fusion, cell damage, membrane genesis, etc. Here we investigate the process of conversion from lamellar into cubic phase during temperature cycling through the lamellar liquid crystalline  $\rightarrow$  inverted hexagonal ( $L_\alpha - H_{II}$ ) phase transition. By means of X-ray diffraction we show that several sodium salts and the disaccharides sucrose and trehalose strongly accelerate the formation of cubic phases in phosphatidylethanolamine (PE) aqueous dispersions. Such acceleration has been observed for dihexadecyl PE (DHPE), dipalmitoyl PE (DPPE) and dielaidoyl PE (DEPE) that do not form cubic phases spontaneously. The degree of acceleration increases with solute concentration and exceeds 100 times at 1 M of solute. Most effective is temperature cycling executed by laser-flash T-jumps. However, the cubic phases produced in this way are less ordered compared to the rather regular cubic structures produced by linear, uniform temperature cycling at 1 - 10 °C/min.

Except for NaSCN, all solutes induce formation of a pure cubic phase in diluted (10 wt %) lipid dispersions, compatible with cubic aspect #8, space group Im3m. In presence of NaSCN, the resulting phase is a mixture of Im3m and Pn3m cubic phases with lattice constants in the ratio 1.28. The pure Im3m phase can be converted into such mixture by heating to about 30 °C above the temperature of the  $L_\alpha - H_{II}$  phase transition, followed by cooling to the range of the  $L_\alpha$  phase. At higher lipid contents (30-50 wt %) the cubic phase formation is hindered at a stage with coexisting cubic and  $L_\alpha$  phases. The cubic phase at this stage indexes as the body-centred Ia3d phase. Heating of the Ia3d phase results in a facile and readily reversible conversion into a mixture of Im3m and Pn3m phases. The lattice constants of the cubic phases do not depend on the temperature in the  $L_\alpha$  region but exhibit strong temperature dependence in the region of the  $H_{II}$  phase. The dimensions of the different cubic phases in the coexistence regions are related to each other in precise accord with the Bonnet transformation between the infinite periodic minimal surfaces describing their geometry. However, no epitaxial relationships appear to exist between the cubic phases and the initial  $L_\alpha$  and  $H_{II}$  phases formed by these lipid dispersions.

## 822.H1 INTERFACIAL METHODOLOGIES FOR STUDYING LIPOLYTIC ENZYME KINETICS

R. Verger<sup>1</sup>, M. Ivanova<sup>2</sup>, S. Ransac<sup>1</sup> and I. Panaiotov<sup>2</sup>

<sup>1</sup>UPR 9025 du CNRS, Laboratoire de Lipolyse Enzymatique, Marseille, France

<sup>2</sup>Biophysical Chemistry Laboratory, University of Sofia, Bulgaria

The growing interest in the mechanisms controlling membrane-bound enzymes has incited a number of biochemists to study in more detail certain aspects of heterogeneous catalysis. In the biological membrane, "immobilized" enzymes act on water-soluble or water-insoluble substrates. Theoretically, heterogeneous catalysis might be studied also using polyamino acids, polynucleotides, or polysaccharides as substrates in insoluble form. These compounds are of biological interest and soluble enzymes hydrolysing them are available in a pure state. Some progress has been made using monomolecular surface films of proteins: these polymers are more difficult to manage *in vitro* than lipids. Recently, the hydrolysis kinetics of poly (D,L - lactide) monolayers spread on basic or acidic aqueous subphase was studied.

The naturally occurring (phospho)lipids are important building stones of the biological membranes. They are water insoluble and spontaneously form lipid-water interfaces such as monomolecular films, bilayers, emulsions, liposomes, or micelles. In addition, a number of soluble enzymes that play an important role in biological events, such as digestion, membrane and cell fusion, lipid, biosynthesis, pinocytoses, etc..., are known and have been isolated in pure form. The fact that it is the substrate that forms an insoluble lipid-water interface makes lipolysis a very attractive system for studies of interfacial enzyme kinetics.

Among the interfacial methods, monomolecular film technology at the air-water interface has been extensively developed and used at our laboratory. With this technique, it is possible to measure and control some important interfacial parameters, such as the surface pressure (interfacial free energy), the molecular area of the substrate, as well as the surface excess of the water-soluble lipases. One prerequisite of the monolayer technique however is that the insoluble monomolecular film of substrate should generate water-soluble products during the reaction process. This is why synthetic medium-acylchain lipids are mainly used as substrates for lipolytic enzymes. We recently developed a new method, using a non-tensioactive agent such as  $\beta$ -cyclodextrin present in the aqueous subphase in order to trap the single long-chain lipolytic products generated during the hydrolysis of monomolecular films of long chain glycerides or phospholipids.

Nevertheless, the question remains as to whether the behaviour of the lipid film at the air-water interface is actually representative of what is occurring either at an oil water interface or in a complex biomembrane. One can gain unique information by measuring the variations in the oil-water interfacial tension ( $\gamma_0/w$ ) as a function of time during lipase hydrolysis. We adapted the well-known "oil-drop method" for use in studying the rate of lipase hydrolysis of natural long chain triacylglycerols. The accumulation of insoluble hydrolysis products at the surface of the drop is responsible for the  $\gamma_0/w$  decrease, which in turn is correlated with changes with time in oil drop profile.

## 823.H1 EFFECTS OF ACYL CHAIN LENGTH AND CHAIN-GLYCEROL LINKAGE ON THE PHASE ORGANIZATION OF LIPID/WATER INTERFACE OF PHOSPHATIDYLCHOLINES: A TIME-RESOLVED FLUORESCENCE STUDY

R. Vladkova, A. Koumanov, R. Koynova and B. Tenchov

*Institute of Biophysics, Bulgarian Academy of Sciences, Acad. G. Bonchev St. bl. 21, 1113 Sofia, Bulgaria.*

Effects of the acyl chain length and chain-glycerol linkage type on the structure and dynamics of lipid head group/water interface in multilamellar dispersions of fully hydrated saturated phosphatidylcholines were monitored by time-resolved fluorescence study using the probe 1-anilinonaphthalene-8-sulfonic acid (ANS). The variation with temperature of the fluorescence lifetime  $\tau_f$ , total fluorescence intensity  $I_0$ , and the relative number of bound ANS molecules  $N_b$  were studied in detail in dimyristoylphosphatidylcholine (DMPC), dipalmitoylphosphatidylcholine (DPPC), distearoylphosphatidylcholine (DSPC) and dihexadecyl-phosphatidylcholine (DHPC). The obtained temperature profiles of the fluorescent parameters clearly exhibit the lamellar gel  $\rightarrow$  rippled gel ( $L_{\beta'} \rightarrow P_{\beta'}$ ) and rippled gel  $\rightarrow$  lamellar liquid crystalline ( $P_{\beta'} \rightarrow L_{\alpha}$ ) phase transitions of these lipids. The values of  $\tau_f$ ,  $I_0$ , and  $N_b$  decrease with

increasing acyl chain length in the series DMPC, DPPC, DSPC. The value of the parameter  $N_b$  depends non-linearly on the chain length in all of the lipid phases  $L_\beta$ ,  $P_\beta$  and  $L_\alpha$ , being about two times larger in DMPC compared to the longer chain lipids. This behavior might reflect conformational changes in the glycerol backbone region upon chain length increase from 14 to 16 C-atoms resulting from a shift in the hydrophilic/hydrophobic balance of the lipid molecule.

The effect of the glycerol-chain linkage type on the bilayer organization was estimated by comparing  $\tau_f$  and  $N_b$  values in DPPC and its ether analog DHPC. Aqueous DHPC dispersions are known to exhibit the phase sequence: interdigitated gel ( $L_{\beta 1}$ )  $\rightarrow$   $P_\beta$   $\rightarrow$   $L_\alpha$ . The interdigitated gel phase  $L_{\beta 1}$  in DHPC was clearly distinguished from the non-interdigitated  $L_\beta$  phase of DPPC by the fluorescence parameter  $N_b$ . The  $L_{\beta 1}$  phase was found to accommodate by 60% more ANS molecules as compared to the  $L_\beta$ . At  $T > T_{pre}$ , the two lipids are indistinguishable with respect of  $N_b$ . The value of  $\tau_f$  is by 40% higher in DPPC in the low temperature gel phase, while in the  $P_\beta$  and  $L_\alpha$  phases this difference is about 15-18%. This is ascribed to a more hydrophilic character of the ester bond as opposed to the ether one, resulting in higher amount of bound water in DPPC compared to DHPC.

This work was supported by grant K-525/95 of the Bulgarian National Science Foundation.

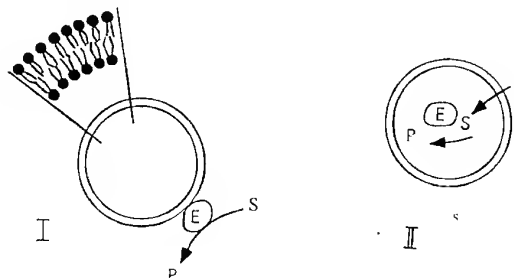
## 824.H1

### ENZYMATIC REACTIONS IN LIPOSOMES

P. Walde, R. Wick, V. Dorovska-Taran, B. Marzetta, P.L. Luisi

*Institut für Polymere, ETH-Z, Universitätstrasse 6, CH-8092 Zürich, Switzerland*

Two different enzymatic reactions occurring in large unilamellar liposomes, composed of 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) have been investigated. In the first case (I), the hydrolysis of POPC catalyzed by phospholipase D has been studied and a new methodology based on  $^1\text{H}$ -NMR spectroscopy was developed. In this case the enzymatic reaction occurs on the surface of the liposomes. In the second case (II), chymotrypsin has been entrapped inside the POPC liposomes, and the hydrolysis of amino acid derivatives which had been added externally to the liposomes was investigated. In this case, the reaction occurs inside the liposomes, and the substrate had to diffuse across the bilayer membrane of the liposomes to reach the entrapped enzyme.



## 825.H1

### PROTEIN CRYSTALLOGRAPHY IN 2D: GRAZING INCIDENCE X-RAY DIFFRACTION FROM PURPLE MEMBRANE PATCHES AT THE AIR/WATER INTERFACE

M.Weygand<sup>1</sup>, S.A.W. Verclas<sup>2,3</sup>, N.A. Dencher<sup>3</sup>, G. Buldt<sup>4</sup>, P. Howes<sup>5</sup>, K. Kjaer<sup>5</sup>, M. Lösche<sup>1</sup>

<sup>1</sup>*Institute of Experimental Physics I, University of Leipzig, Germany*

<sup>2</sup>*Hahn-Meitner Institute (NE), Berlin, Germany*

<sup>3</sup>*Biochemistry Department, TH Darmstadt, Germany*

<sup>4</sup>*Research Center Jülich, Germany*

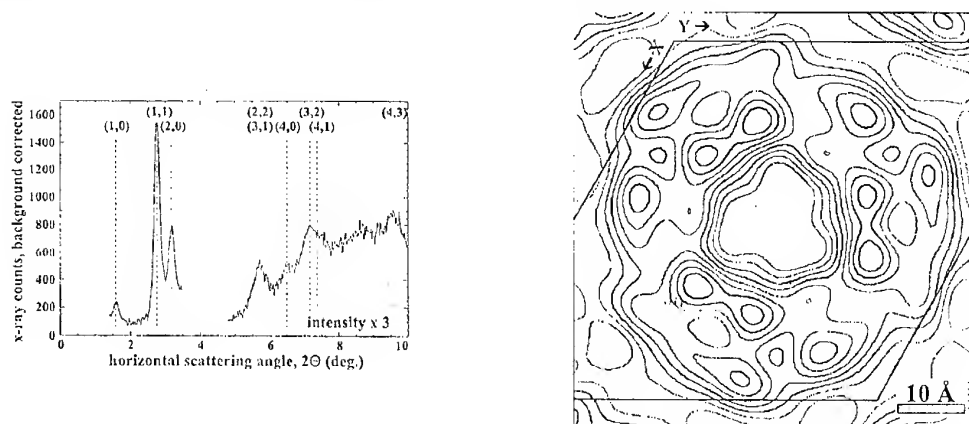
<sup>5</sup>*Department of Solid State Physics, Riso National Laboratory, Denmark*

Purple membrane patches, the protein/lipid crystal films containing bacteriorhodopsin (BR) trimers have been deposited in monomolecular layers at aqueous buffer/air interfaces and characterized with grazing incidence x-ray diffraction (GIXD). While this method is well established for the determination of hexatic and crystalline phases of amphiphilic monolayers at aqueous surfaces, its application to 2D protein crystals is still in its infancy. Our aim is to establish the technique as a new tool for structure determination in the membrane proteins which are not amenable to 3D crystallization.

With native purple membranes deposited on 200 mM KCl subphases we have observed GIXD at various lateral pressures between  $\pi \sim 7$  and 40 mN/m at room temperature. Diffraction peaks up to the 7th order  $[(h,k)=(4,3)]$  of the hexagonal unit cell have been measured, corresponding to a resolution of  $\sim 8$  Å. At

thid resolution, the electron density map constructed with the phases known from electron microscopy<sup>1</sup> shows the typical annular arrangement of the  $\alpha$ -helices in the BR trimer contained within the hexagonal unit cell. The result have been obtained with less than  $10^{13}$  molecules ( $<1\mu\text{g}$  of protein) in the beam. Changes in the structure have been quantified upon compression of the 2D protein crystal at the interface, and from such measurements mechanical properties of the protein have been deduced. Delipidated purple membranes<sup>2</sup> at the buffer/air interface consist of less ordered 2D crystals and have been observed to diffract only up to the prominent (2,0) peak. Nevertheless, a significant distortion of the unit cell with respect to the native purple membrane has been deduced from these data.

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Diffraction intensity ( $Q_z=0^\circ$ ) from native purple membranes at the buffer/air interface (left) and electron density map (right) constructed using phase information from electron microscopy<sup>1</sup>.

## 826.H1 STRUCTURE OF S-PROTEINS IN 2D CRYSTAL SHEETS AT LIPID MONOLAYERS

M. Weygand<sup>1</sup>, M. Schälke<sup>1</sup>, B. Wetzer<sup>2</sup>, D. Pum<sup>2</sup>, U.B. Sleytr<sup>2</sup>, Nicolas Cuvilliers<sup>3</sup>,  
F. Rondelez<sup>3</sup>, P. Howes<sup>4</sup>, K. Kjaer<sup>4</sup>, M. Lösche<sup>1</sup>

<sup>1</sup>Institute of Experimental Physics I, University of Leipzig, Germany

<sup>2</sup>Center for Ultrastructure Research, University of Agriculture, Vienna, Austria

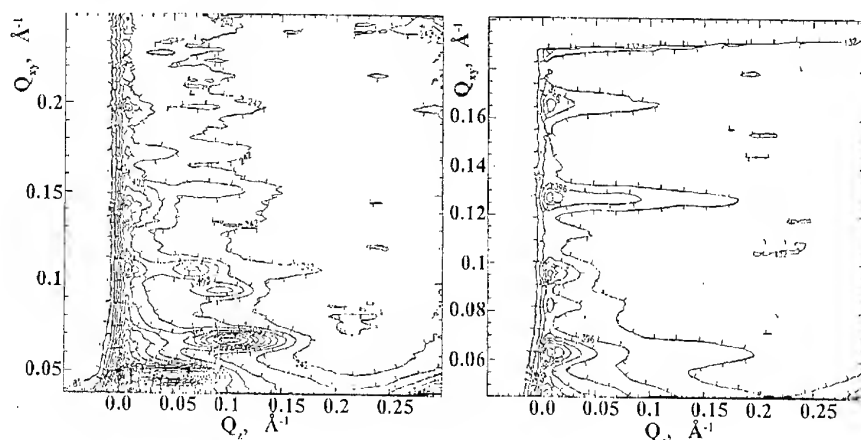
<sup>3</sup>Institute Curie, PC-PSI, Paris, France

<sup>4</sup>Department of Solid State Physics, Riso National Laboratory, Denmark

2D crystalline sheets of S-layer proteins comprise the outermost cell membrane component of a large variety of bacterial cells. We have recrystallized purified proteins from *B. sphaericus* CCM2177<sup>1</sup> and from *B. coagulans* E38-66<sup>2</sup> at phospholipid monolayers and have studied the mutual influence between the lipid and the protein component in such systems using fluorescence microscopy and FTIR spectroscopy<sup>3</sup>. These observations stimulated questions about the structural arrangement of lipid and protein on the molecular length scale, which we have addressed using X-ray and neutron reflectometry and grazing incidence x-ray diffraction (GLXD) of lipid monolayers prior to protein adsorption and of the complexes of the 2D protein crystal and the lipid. In the reflectivity measurement ample use of contrast variation was made, and the data were analyzed using the composition-space refinement approach<sup>4</sup>, which affords a determination of the average structure normal to the interface with high resolution. GIXD of 2D protein crystal sheets at the buffer/air interface is a emerging technique to determine the intrinsic structure of membrane proteins. We have been able to collect data out to  $Q_{xy} \sim 2\pi/8 \text{ Å}$  from protein systems. A comparison of the lipid reflexes taken prior to and after protein adsorption enables a discussion of the rearrangements of the lipid monolayer upon protein crystallization.

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Diffraction intensity contour plots from 2D crystal sheets of the S-layer protein from *B. Sphaericus* CCM2177 (left), and from *B. coagulans* E38-66 (right) underneath DPPE monolayers. Both samples contain  $\sim 10^{12}$  protein molecules within the area encountered by the x-ray beam.

## 827.H1

### ON THE TRANSPORT MECHANISM OF THE SUGAR SPECIFIC OUTER MEMBRANE PROTEIN LamB

M. Winterhalter<sup>1</sup>, N. Saint<sup>2</sup>, and J.P. Rosenbusch<sup>2</sup>

<sup>1</sup>Dept. of Biophys. Chem. and <sup>2</sup>Dept. of Microbiology, Biozentrum, Klingelbergstr. 70,  
CH-4056 Basel, Switzerland

Trimeric maltoporin (LamB protein) facilitates the diffusion of maltodextrins across the outer membrane of Gram-negative bacteria. The crystal structures of maltoporin from *Escherichia coli* in complexes with maltotriose and maltohexaose determined to a resolution of 3.2 and 2.8 Å. They reveal an extended binding site within the maltoporin channel [1]. The hydrophobic face of the sugars are in van der Waals contact with the *greasy slide* which is composed of aromatic residues and guides the sugar into and through the channel constriction. The aromatic residues of the greasy slide (W74, Y6, W420, W358, F227), as well as a tyrosine (Y118) in the channel constriction were replaced one by one by alanine. Purified LamB protein as well as the mutants were reconstituted into artificial planar lipid bilayer and conductivity measurements were performed. Titration experiments with maltotriose and maltohexaose yielded the binding constant for the respective sugars. In addition the spectra of the current noise was analyzed to yield on and off-rates of sugar ligands. The results are discussed with respect to the crystal structure and compared with swelling experiments of liposomes containing reconstituted LamB proteins.

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## 828.H1

### POLYELECTROLYTE-INDUCED REARRANGEMENTS IN THE BILAYER LIPID MEMBRANE

Alexander A. Yaroslavov, Anna A. Efimova, Olga Ye. Kuchenkova, and Elena A. Kiseliyova  
Faculty of Chemistry, Moscow State University, Leninskie Gory, Moscow 119899, Russia

To study the mechanism of polyelectrolyte-cell membrane interaction, a model system, a synthetic polycation - liposomes, was studied. Two polycations, poly(N-ethyl-4-vinylpyridinium bromide) (PEVP) and polylysine (PL), as well as mixed unilamellar liquid and solid liposomes composed of negatively charged diphosphatidylglycerol (cardiolipin, CL) and neutral phosphatidylcholine (PC) were used. The main attention was paid to (1) composition and structure of the polycation-liposome complex, (2) reversibility of

polycation adsorption and (3) reversibility of structural rearrangements in the liposomal membrane induced by polycation adsorption/desorption process.

In the initial liposomes, liquid and solid, negatively charged CL molecules were found to be nearly uniformly distributed between the outer and inner leaflets of the liposomal membrane as well as within each of the leaflet.

Adsorption of both PEVP and PL on the surface of liquid liposome induced lateral segregation in the liposomal membrane. As a result, the initial membrane divided into two microphases: one composed of neutral PC molecules, and other consisting of CL molecules keeping together due to ionic contacts of their negatively charged headgroups with positively charged polycation units. In addition, PEVP caused CL molecules to migrate from the inner to outer leaflet of the membrane (polycation-induced flip-flop). This led to a sharp charge asymmetry in the membrane in contact with PEVP. Polycation adsorption also terminated migration of lipid molecules between liposomes.

When adsorbed PEVP, liposomes retained their integrity unless the content of CL in the membrane exceeded 30 mol%. At higher CL content adsorption of PEVP led to irreversible liposome disruption. On the contrary, when contacted PL, the liposomes remained unchanged at any CL content, up to 100 mol%.

Both polycations could be completely displaced from the liposome surface by recomplexation with the excess of polyanions. As a result, the initial transmembrane and lateral distribution of lipid molecules in the membrane was restored. Displacement of polycations was also followed by resumption of lipid migration between liposomes.

In solid liposomes, only the outer CL molecules were able to form the interfacial complexes with both adsorbed polycations. In this case, adsorption of polycations did not result in lateral segregation and did not induce transmembrane migration of CL molecules, but led to formation of defects in the membrane and increase of membrane permeability. Polycation-solid liposome contact was irreversible: PAA did not displace the polycations from the solid liposome surface.

The structures of complexes formed by adsorbed PEVP and PL on the liposome surfaces as well as possible reasons of different action of PEVP and PL on the membrane of liquid and solid liposomes will be discussed.

The work was in part supported by the Russian Foundation for Fundamental Research (grant 96-03-33725a).

## 829.H1 NANOSECOND FLUORESCENCE OF D1/D2/cyt b-559 COMPLEX

Oliver Zajkov

*Faculty of Natural Sciences and Mathematics, Institute of Physics, P.O. Box 162, 91000 Skopje, Macedonia*

Temperature dependence of the nanosecond fluorescence of D1/D2/cyt b-559 complex is observed. Upon excitation of the sample by 610 nm laser pulse, radical pair  $P^+I^-$  is formed. Duration of the pulse is 7 ns. Deconvolution for all traces at each temperature is done. There is a three component decay for the temperatures between 80 K-180 K. There are slow component (15 ns-25 ns), middle component (1.5 ns-3 ns) and fast component order of magnitude 0.1 ns. All these components have their maximums at 140 K. As it is expected the fast component has very high intensity. This component disappears at temperatures below 80 K, which is probably due to a lowering the gap between the  $P680^*$  and the radical pair. The possibility for forming the triplet state is low and the complex reaches its ground state through the excited state of  $P680$  instead through the triplet state. There is a shift of the fluorescence band upon lowering the temperature: from 681 nm at 200 K to 684 nm at 4 K. The shift for each component is calculated.

## 830.H1 GEOMETRY OF PURPLE MEMBRANES IN AQUEOUS MEDIUM

A. M. Zhivkov

*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The purple membranes (PM) in vivo are violet coloured plates with shape of cylindrically bent elliptical disk. It is widely accepted that the isolated PM are flat and inflexible in aqueous media but there are still not any direct experimental evidence of this concept. The aim of the present study is to determine the geometry of the undisturbed single PM in aqueous media. We have shown that in aqueous suspensions the PM are either cylindrically or spherically bent disks.

The geometry (shape and size) of the PM is studied by two approaches. In the first approach, the experimentally measured value of the inertial radius  $R_g$  is compared to the theoretically calculated value. For this purpose, theoretical expressions for  $R_g$  of cylindrically or spherically bent disk are derived. The experimental value of  $R_g$  is determined by Small Angle Light Scattering method. Electric Light Scattering is used to determine the area of the PM. The angle of the curvature of the membrane is calculated, for both cylindrically and spherically bent PM, from the ratio of the values of  $R_g$  determined by the different methods.

In the second approach, the value of the pH-induced changes of the intensity of light scattered at  $90^\circ$  are compared to those theoretically calculated for cylindrically or spherically bent particles. The light scattering form factor is calculated in the cases of cylindrically or spherically bent elliptical disks. The value of the curvature calculated in this way is in very good agreement to the value obtained by the first approach.

The comparison between the experimental and theoretical value of the intensity of light scattered at  $90^\circ$  for two different wavelengths shows that the PM are cylindrically bent in aqueous media. The conclusion that the PM are bent with the cytoplasmic surface in the outside direction is derived from the comparison of the sign of the pH-induced changes of the curvature of the PM to the literature data for the transmembrane asymmetry of the charge density.

## 831.H2 SHAPE INSTABILITY OF A CELL DRIVEN BY LOCAL SOFTENING OF THE ACTIN NETWORK

A.A. Boulbitch, E. Sackmann

*Dept. of Biophysik E22, TU München, D-85747 Garching bei München, Germany*

Mechanical behaviour of animal cells is determined by their complicated architecture including bilayer membrane with actin sublayer connected to the cell cytoskeleton. The submembranous actin network is inhomogeneous structure. Fluctuations in the process of actin polymerisation, local rupture or local dissolution of the actin network give rise in network holes arising. Several models describe the mechanical behaviour of cells and vesicles. Under the strong cell deformation only the lateral tension making the main contribution should be taken into account<sup>1</sup>, while global shape transformation in vesicles containing no actin network is described by curvature elasticity model<sup>2</sup>. In order to describe local deflections of a cell surface the previous approaches [1,2] is expanded so as to take into account the both contributions. The equation of the local cell membrane deflection is obtained. The latter makes it possible to study the effect of local softening of actin sublayer.

It is shown that local softening of a submembranous actin network followed by local decrease in lateral elastic modulus of the membrane gives rise to cell shape instability. Depending on the place on the phase diagram the latter manifests itself as either an invagination, or a bud. The phase diagram of bifurcation is obtained. It is shown that bifurcation is jumpwise everywhere except the isolated point of soft bifurcation. Estimates show that bifurcation takes place in its vicinity, where it is nearly soft and where the amplitude of a deflection strongly fluctuates with slow kinetics.

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## 832.H2 HETEROCOAGULATION AND ELECTROSURFACE PHENOMENA IN BIOMINERAL SYSTEMS

Estrela-Llopis V.R.

*Institute of Bio-Colloid Chemistry, National Academy of Sciences of Ukraine, Kiev*

High priority of bio-adhesion phenomena in ecology, bio-technology, medicine and the lack of universal approaches to the analysis of its causes. Heterocoagulation as limiting process in bio-adhesion of biological cells to mineral surfaces and particles. Long-range physical stability mechanisms as limiting factors in specific chemical interaction in aqueous systems. Diffuse layer of extracellular metabolites (EMDL) as radical long-range factor distinguishing live colloid objects - biological cells - from mineral

particles. Mechanisms of superlong-range action in biocolloids stability - electrodiffusiophoresis and selective adsorption measurements of particle charge in cell EMDL. Mechanisms mentioned as basis of adaptation of DLVO theory method for biocolloids.

Problem of electrosurface effects and measurements in biological suspensions. Alternative mechanism of superlong-range action - microdipolophoresis of the particle in cell's inherent high-gradient electric field. Cell energy limitations and possibility of technical solution. EMDL and new biotechnologies for metals recovery.

Models of biological cell polarization. EMDL influence on induced cell dipole moment. Influence of trans-membrane ion traffic and multicomponent electrolyte composition on  $\alpha$ -dispersion of dielectrical permeability of cell suspensions. Taking into account of the balance between thickness of cell membrane and boundary layer (layer of immobilized ions in cell double electric layer) as a basis for correct interpretation of cell suspensions stability based on DLVO theory.

## 833.H2

### THE CHARACTERISTIC OF KINETICS OF IMMOBILIZED BACTERIAL BIOLUMINESCENT SYSTEM

Hendogina E.V., Abakumova V.V., Kratasyuk V.A.

*Institute of Biophysics, Krasnoyarsk, Russia*

The co-immobilization into the starch gel of couple enzyme system NADH:FMN-oxidoreductase-luciferase (P-L) and their substrates: FMN, tetradecanal and NADH were conducted. The gel micro-environment appears to be optimal media for luciferase, judging from its high activity and increased stability. The immobilized enzymes existed good thermal stability, the decrease of inactivation rate under the effect of high concentrations of salts and hydrogen ions. The activity yield - more 100%. Time of storing of immobilized R-L with substrates is 60 days at 4°C. The characteristics of bioluminescent reaction such as yield activity and reaction rate for immobilized and soluble R-L have been compared. It is shown that they depend on: 1. effectiveness of inside and outward interactions between components of reaction; 2. diffusion mechanisms; 3. bioluminometers construction. The role of each immobilized substrates on the characteristic of kinetics of R-L has been determined. The microenvironment of co-immobilized enzymes with substrates in starch gel are similar to colloidal conditions in native bacterial to investigate the mechanisms reaction of bacterial bioluminescence.

## 834.H2

### CHARACTERIZATION OF ADSORBED PROTEIN A AND ITS BINDING ABILITY TO IgG

M. Murata<sup>1</sup>, M. Arakawa<sup>1</sup>, M. Morikawa<sup>1</sup>, T. Yoshida<sup>1</sup>, and M. Hato<sup>2</sup>

<sup>1</sup>*Chugai Pharmaceutical Co., Ltd., 5-1-5 Ukima, Kita-ku, Tokyo, 115, Japan*

<sup>2</sup>*National Institute of Materials and Chemical Research, 1-1 Higashi, Tukuba, Ibaraki, 305, Japan*

Recently, many attempts have been made to investigate the structure of the adsorbed proteins and the interactions between them. In this presentation, we report the pH-dependent conformation changes of adsorbed protein A and its binding ability to IgG investigated with a Surface Force Apparatus.

Fig.1 shows effect of medium pH on the force curves between protein A-adsorbed mica surfaces in 100mM of NaCl. The force curve at pH 7.4(○) shows longer-range repulsions, suggesting that protein A takes extended conformation. On the other hand, the force curve at pH 3.1 (□) shifts near to the contact position of the two mica surfaces; the thickness of adsorbed layers decreased even though the amount of adsorption was not decreased. This compression was reversible; the force curve and the layer thickness restored to the original level when the medium pH was adjusted to 7.4 again(▲). This suggests that the protein A molecules adsorbed are extended or contracted depending on the value of pH.

With addition of mouse-IgG to these pre-adsorbed layers at pH7.4(Fig.2 ○), the thickness of the layer increased by about 6-8 nm, equivalent to two IgG molecules, between the surfaces (▲). After that, although these layers were washed with the pure buffers at pH 7.4 or 3.1, the increased thickness was lost only after washing with the solution at pH 3.1 (□). Therefore this phenomenon is attributable to the specific binding of IgG to the protein A layers.



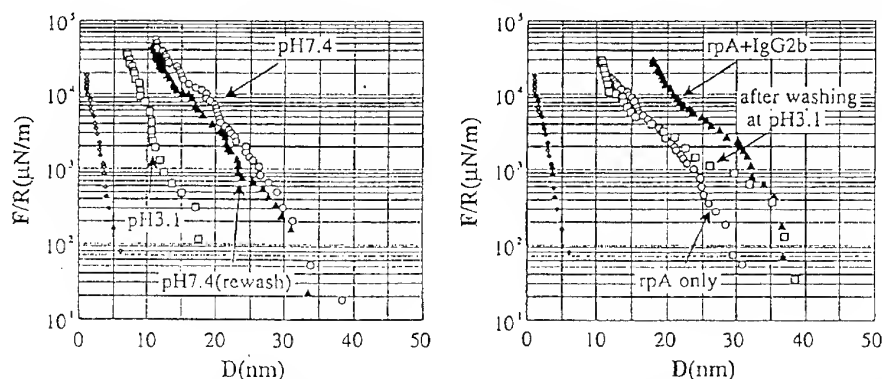


Fig. 1 Forces between surfaces of protein A-adsorbed mica in 100 mM NaCl (pH 7.4 & 3.1) adsorbed mica in 100 mM NaCl (pH 7.4) Fig. 2 Forces between surfaces of IgG2b/protein A-mica in 100 mM NaCl (pH 7.4)

## 835.H2 IMMOBILIZED LUMINESCENT BACTERIA INTO STARCH GEL

Shilova E.V., Abakumova V.V., Rodicheva E.K., Kratasyuk V.A.  
Institute of Biophysics, Krasnoyarsk, Russia.

A possibility of immobilization of luminous bacteria into starch gel have been investigated. It was showed that the characteristics of the light emission of immobilized cells such as light intensity and stability depend on conditions of immobilization: volume and concentration of gel, concentration of cells. Four species of the different strains of luminous bacteria were immobilized. The best object for immobilization were *Photobacterium phosphoreum* (strains 1883,1456) and *Vibrio fischeri* (strain 2088). The conditions of activity storing of immobilized bacteria were studied. We found that the best of storage temperature is 4°C, and immobilized bacteria should be covered by film to protect gel from drying. The optimal conditions have been found to obtain the preparation. The immobilized cells emitted light for more than 70 days. It was showed that immobilized materials may be used for determination of quantity of quinons. So, this method may be used to prepare stable immobilized luminous bacteria for bioluminescent toxicity tests. The advantages of these tests are the rate, the high sensitivity and accuracy.

## 836.H2 ADHESION OF MODIFIED BY TRYPSIN AND GLYCOPHORIN RED BLOOD CELLS

K.D. Tachev<sup>1</sup>, J. K. Angarska<sup>2</sup>

<sup>1</sup>Faculty of Biology, University of Shoumen, 9712 Shoumen, Bulgaria

<sup>2</sup>Faculty of Chemistry, University of Shoumen, 9712 Shoumen, Bulgaria

The influence of both osmolarity of the medium and the membrane modification by trypsin and glycophorin on the adhesion of a single red blood cell (RBC) on glass surface has been studied. The thin liquid film (called by us "adhesion film") formed between a swollen spherical RBC and the flat glass surface was observed in reflected monochromatic light by a metalographic microscope. From the interference patterns of adherent RBC by the micointerferometric technique the film thickness and radius, the contact angle, and the total adhesion energy ( $W_a$ ) of RBC have been calculated. The adhesion parameters of RBC at different osmolarity were obtained observing the same RBC. In this way the effects of the distribution of RBC by age, membrane charge, elasticity and cell size were excluded.

The values of  $W_a$  of untreated cells ranged from  $3 \times 10^{-9}$  to  $6 \times 10^{-9}$  erg. It was found that the deformations of adhered cells at osmolarity in the range from 143 mOsm to 156 mOsm were not concentrated only in a narrow region around the contact line but they were spread out in a broad zone of membrane surface.

The treatment of RBC membrane with trypsin leads to a detachment of some hydrophilic fragments from the membrane glycoproteins. That is why the thickness of the cell glycocalyx and the membrane negative charge decrease. Indeed, the obtained equilibrium thickness of the adhesion film for the trypsin treated cells was smaller than the one of untreated RBC. It was found also that the contact angle and the total

energy of adhesion increased with the osmolarity but to significantly smaller extent than for untreated cells. Possibly the observed effects can be related to the changes of the rheology properties of the cell membrane caused by trypsin.

In the presented study the increasing of membrane charge was achieved by incorporation of additional amount of glycophorin in the membrane. The number of glycophorin molecules ( $2.4 \times 10^7$  molecules per cell) incorporated in the RBC membrane has been determined by fluorescence spectroscopy at  $\lambda_{\text{ex}} = 514$  nm. Fluorescein isothiocyanate (FITC) has been used as marker. The fluorescence labeling has been done in carbonate buffer with pH=9.5 for 1.5 hours. The conjugate FITC-Glycophorin has been separated from non-reacted FITC in the solution by molecular sieve chromatography. Then the concentration of the labeled protein in the sample ( $9.68 \times 10^{-7}$  M) as well as the concentration of the bound FITC ( $3.33 \times 10^{-7}$  M) have been calculated and the molar ratio FITC:Glycophorin was estimated as 1:3. The incorporation of the FITC-Glycophorin conjugates in the RBC membrane was done at pH=4.0. The adhesion parameters of RBC treated with glycophorin as well as their effective diameters were compared with the same parameters of untreated cells. Based on the results experimentally obtained we suggest that the decreased adhesion ability of glycophorin treated RBC is due not only to the increased negative charge of the membrane but it also can be related to the decreased membrane deformability.

### 837.H3

#### CRYSTALLISATION OF PROTEINS ACCOMPANIED BY FORMATION OF A CYLINDRICAL SURFACE

A. A. Boulbitch

*Fakultät für Physik, TU München, Physik-Dept. E-22, D - 85748 Garching bei München, Germany*

In biological objects there is a set of examples of unusual structures arising under crystallisation of certain proteins. Rather than crystallise into a bulk 3D lattice as it usually occurs for all non-organic and for most of the organic materials these proteins form a self-contained cylindrical surface. Crystallisation of organic molecules and especially of proteins is often determined by gently sloping potentials, which enables us to apply in this case the theory of weak crystallisation<sup>1</sup>. Crystallisation should be considered to be weak if the transition from a liquid to a crystal is of the first order, but is rather close to the second order.

Consider a naive example of an aggregation of molecules whose shape in one of the three mutually perpendicular cross-sections is trapezoidal and in the two others it is rectangular. Assume that under the aggregation the nearest molecules are oriented in the same way. These molecules form obviously an arch-like surface with its radius fixed by the size of the trapezoid.

A possibility of formation a self-contained cylindrical lattice under crystallisation of proteins due to the anisotropic (trapezoidal) shape of their globules is discussed theoretically. The theory of cylindrical crystallisation is considered. It is shown that the list of the low-symmetry phasees is completely determined by the symmetry of the cylinder in this case. The phases symmetries and structures are found out. The phase diagrams are obtained.

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### 838.H3

#### SPECIFIC FEATURES OF BIPHASIC BINARY SYSTEMS: APPLICATION TO PHOSPHOLIPID/WATER MIXTURES

G.G. Chernik

*St. Petersburg State University, Department of Chemistry, St. Petersburg, Russia*

Lipid/water mixtures of high water content have been traditionally described as one-component systems; in most investigations of phase transitions in lipid/water systems experimental results are discussed in such a way as if the properties of the lipid only are measured. Actually, a mixture containing water and a pure synthetic phospholipid is a binary system, and the Phase Rule can be applied to it in a straightforward manner [1]. In a wide concentration range these mixtures are biphasic; in the interpretation of calorimetric

and volumetric measurements one should take into account the specific features of biphasic binary systems. If the phase boundaries of a biphasic binary system are not vertical, heating of the system leads to continuous changes in composition of the phases; the redistribution of components between phases leads to a contribution into such properties as the heat capacity and thermal coefficient of expansion of the biphasic system.

In the studies of phase transitions in aqueous lipids it is a common practice to apply mechanical shear. Procedures of the sample preparation most often include heating to the temperatures of the liquid crystalline lamellar phase existence and the subsequent vortexing, shaking in a mixer, centrifuging many times through a narrow constriction or passing through a hypodermic needle to break up larger particles. As the lipid/water mixtures of high water content are biphasic, these procedures may lead to formation of an irreversible colloidal structure which may be long-lived due to extremely low solubility of lipids in water. One must be aware that the macroscopic properties of the system in this state, like heat capacity (in particular in the vicinity of the transition temperature), temperatures and enthalpies of phase transitions may differ from those of the equilibrium system in which macroscopic phases coexist.

I. G.G. Chernik. *Adv. Colloid Interface Sci.*, 61 (1995) 65-129.

### 839.H3

#### PECULIARITIES OF STRUCTURE FORMATION IN AQUEOUS POLYSACCHARIDES SOLUTIONS

**E.V. Datskevich, L.D. Kachanovskaya, and V.S. Sperkach**

*Institute of Bio-Colloid Chemistry of National Academy of Sciences of Ukraine,  
Joint Laboratory of Medical Physics and Biocolloidal Systems, Kiev, Ukraine*

All physicochemical processes, which are taking place in liquids, could be considered as an aggregate of a large number of superfast reactions of format ion and breakage of intermolecular bonds.

The present work deals with studies of equilibrium in reactions of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Cd}^{2+}$  ions binding with saccharose, dextrin and dextran molecules. Constants of association for the systems indicated at different temperatures have been determined and tabulated. Taking into account the results obtained, peculiarities of structure formation in aqueous solutions of polysaccharides before and after introduction of metal cations into the system have been revealed using the acoustic spectroscopy method. The systems studied display complex temperature and concentration dependencies of the acoustical spectra with three separate relaxation processes being observed. The formation of the complexes has no influence on the static equilibrium structure of polysaccharide molecules, while changing perceptibly their dynamic properties.

Comparison of the results obtained enables us to reach a conclusion on heterogeneous organization of macromolecular structure in the aqueous solutions of polysaccharide : Me : water complexes. Water is present in the system both as a bulk phase of a free solvent, and as a bound water of hydration shells, its state being determined by interaction with the less mobile structure formed by molecules of biocomplex.

### 840.H3

#### A STUDY OF THE INTERFACIAL REACTIONS BETWEEN BIPHASE CALCIUM PHOSPHATE CERAMIC, CIPROBAY AND BACTERIAL STRAINS - IN VITRO APPROACH

**Elena Dyulgerova<sup>1</sup>, Ginka Opalchenova<sup>2</sup>**

<sup>1</sup>*Stomatological Faculty, High Medical Institute, 1 Georgi Sofiisky str., Sofia, Bulgaria,*

<sup>2</sup>*National Drug Institute, 26 Yanko Sakazov blvd., 1504, Sofia, Bulgaria,*

The paper discusses the results of an experimental study on the effect of Biphasic Calcium Phosphate Ceramic on some standard bacterial strains as well as on laboratory isolated polyresistant Gram-negative bacteria. The results show a significant antimicrobial effect of the ceramic manifested during a direct contact with bacteria. In addition, antibacterial activity of Ciprobay was determined by a time-kill curve method and after that the antibacterial activity of Biphasic Calcium Phosphate Ceramic and Ciprobay combinations was investigated in Saline Test Solution. The combination showed an additional killing effect in comparison of

Biphase Calcium Phosphate Ceramic or Ciprobay alone. The surface reactions probably were influenced by the composition of the ceramic and the chemical constituents of the surrounding media.

### 841.H3

#### RAMAN SPECTROSCOPY OF THE INTERACTION OF *CHLORELLA VULGARIS* BIOPOLYMERS WITH THE PARTICLES OF COLLOID GOLD, NATURAL SILICA, AND HEAVY METAL IONS

Estrela-Llopis V.R., Klimovich V.V., Yurkova I.N.

*Institute of Bio-Colloid Chemisty, National Academy of Sciences of Ukraine*

Earlier we have found that the determining influence on the selective interaction show the extracellular metabolites, in particular, external cellular polysaccharides (ECPS) in the phenomenon of the selective heterocoagulation of microorganisms with the colloid particles of precious metals in the presence of the aluminosilicate and silica particles.

The nature of the chemical bonding of ECPS *Chlorella vulgaris* LARG-3 with the particles of the sols of gold, natural silica as well as in connection with the biosorption with metal ions from  $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ;  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ;  $\text{AgNO}_3$ ;  $\text{SrCl}_2 \cdot 4\text{H}_2\text{O}$  solutions with the concentration of  $20 \text{ mg/dm}^3$  was investigated by the Raman spectroscopy method.

It was shown that for all metals including colloid gold the characteristic peculiarity is the interaction on the carboxyl ionized groups typical for polysaccharides. The character of the ECPS spectrum change in the presence of the natural silica allows to conclude that the ECPS adsorption in the given case has mainly the physical character in contrast to the investigated regularities of the given biopolymer on the gold sol. These results explain the regularities of the change in the  $\zeta$ -potential of the colloid gold and natural silica during the ECPS adsorption where in the first case the adsorption results in noticeable decrease in charge but in the second one it does not take place.

It is shown that the change in the band intensity in the  $500\text{-}600 \text{ cm}^{-1}$  region typical for the O-Me bond follows the regularities of the transition of the metals under investigation from the covalent to ionic bond type with FCPS in the row:  $\text{Au} > \text{Ag} > \text{Cu} > \text{Cd} > \text{Sr}$ .

In connection with the influence of the degradation of the investigated mutant strain *Chlorella vulg.* LARG-3 on the heterocoagulation with the colloid gold and the biosorption of  $\text{Au(III)}$  the comparison of the spectra in region of the valence C-H and C-C ECPS oscillations derived in different years was carried out. The change in the initial (as compared with older samples) conformation of the polymer chains that results in the appearance of additional steric impediments during the interaction on the corresponding C-H and C-C groups was shown. This data together with the electrokinetic data concerning the decrease in the effect of the ECPS charge neutralization permits to explain the gradual decrease in the *Chl. vulg.* interaction with colloid and ionic gold (heterocoagulation and biosorption) with the increase in the strain operation period.

The performed comparison of the spectra of the studied metals interaction with general extracellular biopolymers and the separated ECPS from them has confirmed the conclusion concerning the determining role of ECPS in the given process by the example of the investigated microalgae.

### 842.H3 MONOLAYERS OF CORYNOMYCOLIC ACIDS AT WATER-AIR INTERFACE

Tomiko Fujii, Rika Yuasa, and Tokuzo Kawase

*Faculty of Human Life Science, Osaka City University, Osaka, Japan*

Corynomycolic acid (2-alkyl-3-hydroxy fatty acid) produced by *Corynebacterium lepus* is a mixture of homologies having different alkyl chain length. Then ten kinds of 2-alkyl-3-hydroxy fatty acids ( $\text{Rm-CH(OH)-CH(Rn)-COOH}$ ) having definite alkyl chain lengths were chemically synthesized to study the effects of alkyl chain length and the difference of the length of two alkyl chains on monolayer at water-air interface.

The hydrophobic interaction between the two alkyl chains is essential for the monolayer. The most stable condensed monolayer is formed when the total carbon numbers of the two alkyl chains are 25 or more and the difference of the length of the two alkyl chains ( $m-n$ ) is one. While syn-isomers form the condensed

monolayer, anti-isomers normally do not form it. However, anti-isomers may also form the condensed monolayer when the alkyl chain at carboxyl group (the 2-position) is longer than alkyl chain at hydroxy group (the 3-position).

The fact that the critical area of the monolayer of Corynomycolic acid is about  $0.40 \text{ nm}^2$  per molecule proves that carboxyl group and hydroxy group are on the interface to form the monolayer as bipolar substances.

### 843.H3

#### ADHESION OF PLATELETS AND STRUCTURES OF MEDICAL SEGMENTED POLYURETHANE

Fuky V.<sup>1</sup>, Galaeva T.<sup>1</sup>, Severianova M.<sup>1</sup>, Tarasevich B.<sup>2</sup>

<sup>1</sup>*Medicon Ltd, Moscow,*

<sup>2</sup>*Moscow State University, Chemical Department, Russia*

Hemocompatibility of the segmented polyurethane (SPU) is connected with their microphase segregation and alternation of polar and nonpolar fragments on their surface. The formation of such fragments (domains) is conditioned by availability of hydrogenous bonds (H-bonds) between =NH groups and carbonyl oxygen or alkoxy oxygen of urethane fragment (hard block). H-bonds can occur also between =NH groups of urethane group and either polyoxytetramethylenglycol (soft block). Hydrogenous bonds in SPU were studied by IR-spectroscopy. As the criterion of hemocompatibility we used the Relative Index of Platelets Adhesion (RIPA). RIPA is the ratio of quantity of platelets adhesived on the polymer film surface to that on the control glass surface. Material with  $\text{RIPA} < 1$  is considered hemocompatible, while  $< 0.8$  is very hemocompatible. In this work it was found that alteration of SPU H-bond structure correlates with their hemocompatibility. Decrease of quantity of linked H-bonds carbonyl groups with decrease of platelet adhesion, while polar and dispersion components of the surface energy may alterate insignificantly. There is correlation between H-bond structure in SPU and hard domains structure, size and its distribution in the soft oligoether matrix. The following factors influence on H-bond-character, domain structure in SPU and consequently its hemocompatibility: 1) thermotreatment temperature of SPU-article, which contacts with blood, 2) introduction of additional polymer component which forms separate phase in SPU-matrix, 3) external medium polarity on the border of phase division polymer surface - external medium. Last factor ought to take into consideration especially as blood is the polar fluid and SPU-structure alternation by contact with blood perhaps is the essential reason for its hemocompatibility. In order to decrease polar component ( $E_p$ ) of the surface energy and platelets adhesion we introduced in SPU the polyurethane polymer in which the soft phase was polydimethylsiloxane (SPU-Si). It was found that  $E_p$  decreases in 1.5-2 times at SPU-Si concentration of 0.5-3%. However tendency to platelets adhesion decreasing was observed with growth of SPU-Si concentration until 1.0 % while further increasing of SPU-Si concentration led to the growth of platelets adhesion in 4 times in spite of  $E_p$  was invariable. Concerned effect was confirmed by adhesion of model compound to the surface of SPU - SPU Si composites. Such behavior of SPU and SPU - composites testify that the microphase structure is the main factor for the platelets adhesion of polymer systems but not summary surface energy. Microphase division may be regulated by introduction of additional polymer component with creation of composites with different surface energy, physico-chemical and physico-mechanical characteristics.

### 844.H3

#### EFFECT OF THE CHEMICAL MODIFICATION OF THE ARGINYL RESIDUE IN SILK FIBROIN ON THE ATTACHMENT AND GROWTH OF FIBROBLAST CELLS

Yohko Gotoh<sup>1</sup>, Masuhiro Tsukada<sup>1</sup>, and Norihiko Minoura<sup>2</sup>

<sup>1</sup>*National Institute of Sericultural and Entomological Science, Tsukuba, Ibaraki 305, Japan*

<sup>2</sup>*National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan*

Silk fibroin (SF) is a structural protein produced by the *Bombyx mori* silkworm. SF has been recently applied as a biomaterial and a medical material such as an enzyme-immobilization material, an oral dosage form, and a burn wound dressing because of its unique physicochemical properties (1). We have observed

that cell attachment and growth on SF were comparable to those on collagen, and it is anticipated that SF will be used as a cell culture substrate (2). Recently, the partial primary structure of SF has been determined (3). The structure reveals that the carboxy-terminal nonrepetitive region of SF contains many basic amino acid residues, especially, arginyl residues (3). Because cells have a predominantly negative charge on their surface, the arginyl residue having a positive charge in SF is expected to play an important role in the interaction between cells and SF.

We have reported that the positive charge of the arginyl residue was masked by a chemical modification of the arginyl residue using 1,2-cyclohexanedione (CHD) in aqueous alkaline medium (4). In this study, we prepared the matrices of SF with different degrees of modification of arginyl residues by the reaction between CHD and SF. Two kinds of SF, namely native SF (NSF) obtained from the silk gland of the silkworm larvae and regenerated SF (RSF) prepared from cocoons of the same silkworm, were used, because their amino acid compositions were slightly different from each other. The attachment and growth of mouse fibroblast (L-929) cells on the matrices of the modified NSF and RSF were studied using a cell culture method in order to clarify the role of the basic arginyl residue of SF during cell attachment and growth. It was observed that the chemical modification of the arginyl residue in RSF restrained the cell attachment, while the modification in NSF promoted the cell attachment. However, the modification did not significantly affect the cell growth on both NSF and RSF.

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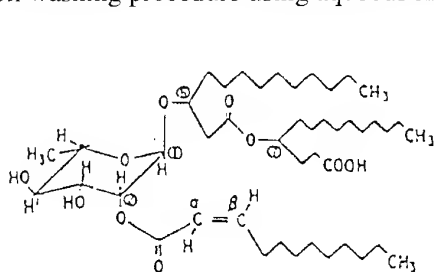
### 845.H3 MULTIFUNCTIONALITY OF RHAMNOLIPID -TYPE BIOSURFACTANTS AND THEIR APPLICATION

Y. Ishigami<sup>1</sup>, K.J. Hong<sup>2</sup>, Y.K. Choi<sup>2</sup>, T. Kajiuchi<sup>2</sup>

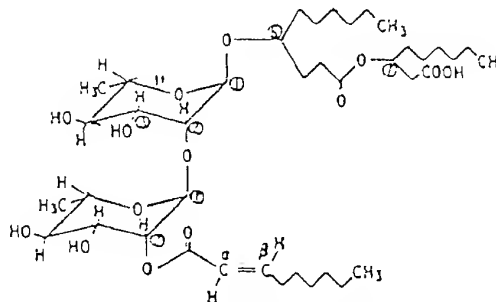
<sup>1</sup>National Institute of Materials and Chemical Research 1-1, Higashi, Tsukuba, IBARAKI 305, Japan

<sup>2</sup>Tokyo Institute of Technology, Dept. of Environmental Chemical and Engineering, 4259, Nagatsuta-cho, Midori-ku, Yokohama 226, Japan

Rhamnolipid A and B are produced microbially in inorganic media from ethanol as the sole carbon source using *Pseudomonas* BOP 100. Basic function of rhamnolipids is to take hydrocarbons inside microbial cells. Therefore, they show excellent surface activity in alkaline conditions in spite of their bulky (interdigitating) molecular structure. This result may be attributed to the multifunctionality of rhamnolipids consisting of double or triple hydrophilic moieties (saccharide and carboxylic residues) and triple alkyl chains as shown in the chemical formula. It is notable that rhamnolipid A and B organized vesicle in the weak acidic condition transitionally from micelle formation in the alkaline condition. From the standpoint of their large biodegradability, complexation with heavy metals and dispersing actions, it was found that rhamnolipids was effective for the removal of hazardous heavy metals from contaminated soil by means of a soil washing procedure using aqueous rhamnolipid solutions.



Rhamnolipid A (R-A)



Rhamnolipid B (R-B)

### 846.H3 SCANNING PROBE MICROSCOPY STUDIES OF AGGREGATION IN ULTRA THIN ORGANIZED ORGANIC FILMS

George R. Ivanov<sup>1</sup>, Masamichi Fujihira<sup>2</sup>, Hajime Takano<sup>2</sup> and Yoh Okabe<sup>2</sup>

<sup>1</sup>*Institute of Solid State Physics, BAS, and Advanced Technologies Ltd.,*

*Postoyanstvo str., bl. 253/E, BG-1111 Sofia, Bulgaria,*

<sup>2</sup>*Department of Biomolecular Engineering, Tokyo Institute of Technology,*

*4259 Nagatsuta, Midori-ku, Yokohama 226, Japan*

In the last 8 years we systematically investigate insoluble monolayers at the air-water interface and ultra thin organized organic films deposited as Langmuir-Blodgett (LB) films from dipalmitoylphosphatidylethanolamine head labeled with nitrobenzoxadiazole (DPPE-NBD) because this compound seems suitable as a model molecule for understanding aggregation and energy transfer processes. For the first time a fluorescence self-quenching in Langmuir films was observed [1] for this molecule. This allows high contrast fluorescence microscopy both at the air-water interface and on LB film. For better understanding of the condensed phase we deposited LB multilayers from DPPE-NBD in the condensed state and studied them with ellipsometry, small-angle X-ray diffraction and polarized FTIR spectroscopy [2]. Well-ordered films with monolayer thickness of around 3.0 nm, tail tilt of 20° from the normal to the substrate and benzene ring plane normal to the substrate were achieved. The same result was obtained by computer-aided molecular conformation analysis.

Recently the ability to distinguish between different phases was shown for scanning force microscopes [3]. Observations with fluorescent microscopy, atomic force microscopy (AFM), friction force microscopy (FFM) and scanning surface potential microscopy (SSPM) [4] reveal clear pictures of the liquid-solid phase coexistence and of domain merging at high pressures. The AFM and FFM show submicron domains which are present since the beginning of the liquid expanded - liquid condensed phase transition together with the bigger domains. Upon compression the defects seem to remain in the liquid phase between the merging domains and even at highest pressures circular regions composed of liquid phase and needle-like 200 nm wide multilayer structures remain. The difference in height between the solid and the liquid phase was measured to be around 1.6 nm. Surprisingly multilayer (mainly bilayer) aggregates are observed at pressures much lower than the equilibrium spreading pressure. Variations of the water subphase content, temperature and the deposition conditions change the aggregation and the fluorescence self-quenching.

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### 847.H3 LYOPHILIZATION OF INTERFACE IN AQUEOUS SOLUTIONS OF BIOMACROMOLECULES

L.D. Kachanovskaya, L.P. Sinchuk and F.D. Ovcharenko

*Institute of Bio-Colloid Chemistry of National Academy of Sciences of Ukraine,*

*Joint Laboratory of Medical Physics and Biocolloidal Systems, Kiev, Ukraine*

In this work, certain physicochemical properties of aqueous solutions of collagen, which have been preliminarily lyophilized by interfacial polymeranalogous transformations method, as well as properties of the films prepared from such solutions.

Electron microscope studies of the structure of dried collagen film have shown that it consists mainly of fiber-like formations constructed from cylindrical fibrillae having diameter from 5 to 20 nm. Collagen fibers comprise bundles of parallel fibrillae with alternately interlaced chaotically aggregated biomacromolecules. It was established in the studies of aqueous solutions of collagen and tropocollagen that the pyrrolidinic rings of aminoacids possess peculiar stereochemical properties, which restrict flexibility of the chain, while all aminoacid functional groups are situated on the external side of biomacromolecule.

In order to destroy the gel structure of the aqueous solutions of collagen and its preparations, partial lyophilization of interface has been carried out by modification of tropocollagen chain or its fragments through inter-fibrillar linking of grafted methylolpolyamide or polyethyleneglycolpyrrolidone chain links. Lyophilization of the interface results in somewhat diminished fibrillar mobility, while orientational effects in the film being dried are intensified simultaneously.

### 848.H3

#### FORMATION, PROPERTIES AND APPLICATIONS OF SURFACE-ACTIVE PROTEINS

Shlomo Magdassi

*The Casali Institute of Applied Chemistry, School of Applied Science and Technology,  
The Hebrew University of Jerusalem, 91904 Jerusalem, Israel*

Protein molecules are composed of various hydrophobic and hydrophilic groups, which may contribute to their adsorption at interfaces. Their surface activity is controlled by both electrostatic and hydrophobic interactions, as well as by their structural properties.

Proteins with improved surface activity may be formed by covalent attachment of various hydrophobic groups. The resulting proteins, as will be demonstrated, have better foaming and emulsification properties, as well as improved adsorption at various interfaces, than the native proteins.

Biologically active proteins, such as enzymes and antibodies, can be used in unique applications, if they are converted into surface-active proteins. For example, surface-active antibodies may be adsorbed on emulsion droplets, leading to a new drug targeting system, or may form colloidal immunoclusters, which can be used in immunodiagnostics.

Enhancement of protein surface activity may also be achieved by interactions with classical monomeric surfactants. The properties of protein-surfactant complexes will be discussed as well as their use in flocculation and microencapsulation processes.

### 849.H3 SURFACTANTS IN THE TECHNOLOGY OF BIOMATERIALS PRODUCTION

V.G. Praydin<sup>1</sup>, V.G. Germashev<sup>1</sup>, L.S. Nesinevich<sup>1</sup>, V.V. Malkina<sup>2</sup>

<sup>1</sup>*The Biochemical Factory, Scientific Center, Shebekino, Russia*

<sup>2</sup>*NPAO "SintezPAV, Shebekino, Russia*

Determinative step in biotechnology is the isolation of the goal product from the biomass. One of the isolation methods is the reaction of the biocomponent with surfactants. For example, it is a known method to isolate lysine by binding it into ion compound with alkylbenzene sulphonic acid by amino groups reaction (N-complex). Here the sediment isolation temperature is not critical. In the proposed paper the reaction of lysine with sodium dodecyl sulphate (and with other alkyl sulphates) was studied, ionic N-complexes and crystalline complexes formed at the cost of the carboxylic group hydrogen bond (H-complexes) were isolated, and their colloid-chemical properties were investigated. The complexes were detected and isolated using crystallization separation based on the difference of Krafft temperatures. Depending on conditions, the involvement of lysine in the complex is 55 -70%. Optimum temperature regions for the existence of the complexes were defined. The isolation of lysine on the basis of an H-complex is advantageous, since it is sufficient to change temperature and pH-value for its decomposition, i.e. for the liberation of lysine. The method can also be used in some other biotechnological processes, as well as in the manufacture of medicines, vitamins and others. To clarify the lysine-dodecyl sulphate reaction mechanism, the dodecyl sulphate solutions were studied in the presence of caproic, lauric and stearic acids, the corresponding H-complexes were detected and isolated and their colloid-chemical properties were investigated. The H-complexes of lysine with dodecyl sulphate can be used not only in biotechnology, but they also have an independent importance as new surfactants, i.e. the formation of H-complexes can be considered as a method of introduction of a long-chain structural fragment with the formation of new surfactants including bio-surfactants.



### 850.H3 SURFACTANTS IN THE TECHNOLOGY OF BIOMATERIALS PRODUCTION

V.G. Pravdin<sup>1</sup>, V.G. Germashev<sup>1</sup>, L.S. Nesinevich<sup>1</sup>, V.V. Malkina<sup>2</sup>

<sup>1</sup>The Biochemical Factory, Scientific Center, Shebekino, Russia

<sup>2</sup>NPAO "SintezPAV, Shebekino, Russia

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### 851.H3

#### THE DISTRIBUTION OF CAROTENOIDS IN MODEL INTESTINAL LIPID SYSTEMS

Gillian T. Rich, John Leney and Annette Fillery-Travis

*Institute of Food Research, Norwich Research Park, Norwich. UK NR4 7UA*

In recent years there has been an increasing awareness that naturally occurring carotenoids in plant food sources have potential beneficial effects on human health for their antioxidant and anti-carcinogenic properties. Critical steps in the current model of transport of these lipid-soluble micronutrients from the diet to the body tissues takes place in the gastrointestinal tract. Here, transfer of carotenoids to the point of absorption involves partitioning between a series of dynamic colloidal phases including emulsion droplets and micellar aggregates. In this paper we have modelled the lipid phases present in the gut and determined the factors influencing partitioning of carotenoids from tissue to emulsion and onto the micellar phase. In particular we have investigated the interfacial/core distribution of carotenes within the emulsion phase and its influence on partitioning to the micellar phase. The presence of lipase activity at the emulsion has been shown to influence this process significantly and possible mechanisms for this effect are discussed. Other factors that determine the bioavailability of carotenes namely pH, the carotenoid carrying capacity of mixed micelles as a function of their composition and the role of saliva are also addressed.

### 852.H3

#### THE ROLE OF CHOLESTEROL IN SURFACTANT

D. Palmer<sup>1</sup>, F. Green<sup>1</sup>, O. Lopatko<sup>2</sup> and S. Schürch<sup>1</sup>

<sup>1</sup>Respiratory Research Group, The University of Calgary, Alberta T2N 4N1 Canada

<sup>2</sup>Department of Physiology, University of Adelaide, Australia.

Pulmonary surfactant contributes to lung stability by lowering the surface tension in the alveolus. Surfactant is composed of a mixture of lipids including cholesterol and specific proteins. Dipalmitoylphosphatidylcholine (DPPC) is the primary phospholipid and is capable of lowering the surface tension in the alveolus to near zero values. Cholesterol is a neutral lipid and its role in the surface tension requirements of the lung is unclear. It is thought that cholesterol may play a role as a fluidizer to enhance the adsorption and

respreading of DPPC. Current preparations of synthetic surfactants do not contain cholesterol. Cholesterol occurs naturally in surfactant and is present in concentrations of 4-7%. Previous studies have shown that cholesterol in the absence of surfactant-associated protein A (SP-A) destabilizes films of lipid extract surfactant under compression and impairs the surface tension lowering ability of surfactant. The purpose of the current study was to investigate the effects of cholesterol on the surface properties of surfactant. Using the captive bubble technique, and bovine lipid extract surfactant (bLES) with concentrations of 2.5, 5 and 10% cholesterol, we found that cholesterol enhanced the rate of surfactant adsorption into the air-liquid interface. Films of bLES reached a plateau value of  $\sim 25$  mN/m in approximately 5 seconds. With the addition of 10% cholesterol, films reached a plateau value of less than 24 mN/m in substantially less time (approximately 0.1 second). In contrast to previous results, we also found that cholesterol had no measurable effect on the stability of the bubble at low surface tension, and did not inhibit films of bLES from reaching low surface tension values. In addition, films of bLES with 10% cholesterol required less area compression (12% versus 16%) to reach near zero minimum surface tension (reduced film compressibility). These preliminary results indicate that cholesterol does not interfere with the ability of the film to reach low surface tension and cholesterol appears to promote refinement towards a pure DPPC film.

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### 853.H3 FOAM FILMS OF ALCOHOLIC SOLUTIONS OF GLYCOPROTEINS

J. Senée<sup>1</sup>, B. Robillard<sup>2</sup> and M. Vignes-Adler<sup>1</sup>

<sup>1</sup>Laboratoire des Phénomènes de Transport dans les Mélanges du CNRS, 4ter,  
Route des Gardes, F 92190 Meudon, France

<sup>2</sup>Laboratoire de Recherche Moët & Chandon, 20, Avenue de Champagne, F-51205 Epernay Cedex, France

Foams and emulsions stabilized by macromolecules are of considerable importance in the field of food industry. Beers and sparkling wines are celebrated examples of foaming biological liquids: the former foams are quite stable whereas the latter ones are transient. The link between the foam film lifetime and the overall foam stability has long been stated. In this context, we have investigated the drainage kinetics and stability of horizontal foam films in relation to the foam stability of alcoholic solutions of glycoproteins as a model for sparkling wines. Experiments were made with an exogeneous glycoprotein, the Maltosyl Bovine Serum Albumine (MBSA) and an endogeneous one, a yeast glycoproteins mixture (YG) obtained by an alcoholic fermentation: these 2 proteins differ by their sugar content and the aminoacids quality, and by their history with respect to the alcohol. Major result is that a MBSA film exhibits formation and expansion of black spots of less thickness ( $\approx 20$  nm) in the film during drainage while the YG films thin continuously until to be as thin as a black film ( $\approx 15$  nm). Surface pressure of both solutions was very low, particularly for the YG one ( $< 1$  mN/m). However, MBSA films are far less stable than YG films at concentrations lower than 10 mg/liter. The stepwise decrease of the MBSA films is typical of a stratification effect as in micellar solutions: it exists apparently an aggregation and a structuration of the glycoproteins because of the newly created interactions with the ethanol, what generates destabilizing vacancies inside the film. The YG endogeneous proteins are well adapted to the alcoholic solution and they remain unfolded inside the film preventing its collapse. No clear correlation could be found between the films and foams lifetimes: it was assigned to the gravity drainage which could not be counterbalanced by interfacial stresses.

### 854.H3 THE INFLUENCE OF PROTEINS ON THE CALCIFICATION OF TITANIUM IMPLANTS STUDIED BY DYNAMIC CONTACT ANGLE ANALYSIS

Ana Paula Serro, Anabela Catarino Fernandes and Benilde Saramago

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico,  
Av. Rovisco Pais, 1096 Lisboa Codex, Portugal

The spontaneous formation of a calcium phosphate layer on the surface of titanium implants in contact with biological model fluids has been investigated by several groups [1,2] since it is an important step towards the osseointegration of this material. However the effect of the presence of proteins in the real biological fluids on the process of deposition of this apatite-like layer is not well understood yet. In this work

the process of calcium phosphate deposition on titanium surfaces in contact with bovine serum albumin (BSA) dissolved in Hank's Balanced Salt Solution (HBSS) is studied by dynamic contact angle analysis (DCA). Previous wettability and XPS studies [3] indicate that the formation a calcium phosphate layer does occur in the presence of albumin. The present DCA studies indicate that calcium phosphate precipitates over a layer of previously adsorbed albumin on the titanium surface and, conversely, the presence of an apatite-like layer on the titanium does not prevent the adsorption of protein molecules. When the bare titanium substrate (covered by  $\text{TiO}_2$ ) contacts a solution where both the protein and the calcium and phosphate ions are present, all the species will adsorb at the surface. DCA analysis seems to indicate that there is an initial deposition of the ions followed by the protein adsorption. Further studies of the time evolution of the calcium and protein concentrations in the solution and the protein content at the surface will be performed to confirm this hypothesis.

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### 855.H3 ROLE OF THE DIFFUSIONAL FACTORS ON ACTIVITY OF ENZYME IMMOBILIZED BY BILAYER PHOSPHOLIPID VESICLES

Yury E. Shapiro, A.V. Smirnova

*Bogatsky Physico-Chemical Institute, National Academy of Sciences, Odessa, Ukraine*

By enzyme immobilization inside the phospholipid liposomes the substrate and product molecules penetrate the phospholipid bilayer in the opposite directions. Therefore the diffusional factors may exercise the great influence on the enzymatic kinetics.

The kinetic parameters for enzymatic hydrolysis of a classic substrate, *p*-nitrophenyl acetate, in presence of  $\alpha$ -chymotrypsin immobilized, and non-immobilized by phospholipid bilayer liposomes are essentially differed. As it was shown previously, the spontaneous hydrolysis of a substrate does not insert errors into activity parameters for  $\alpha$ -chymotrypsin. An immobilization was carried out by the co-sonication of the aqueous solution of enzyme and the buffer dispersion (pH 7.5) of the multilayer liposomes. An enzyme non-immobilized by liposomes has been separated using gel-filtration on Sefadex G-50. According to the light scattering data the average outer diameter does not change after the enzyme inclusion, and it is equal to  $(42 \pm 3)$  nm.

As it has been shown using the integral form of the Michaelis-Menten equation according to the Foster-Neemann method, the immobilization of  $\alpha$ -chymotrypsin tends to increase of the value of Michaelis constant,  $K_m$ , and decrease of the value of maximum rate,  $V_{max}$ , by a factor of 2.3. One can assume that these exchanges are conditioned either by the non-competed inhibition of enzyme by phospholipid molecules, or by reduction of a rate of the enzyme-substrate complex formation. These distinctions are conditioned by diffusional hindrances arisen with immobilization of enzyme. Indeed, the value of appropriate Michaelis constant,  $K_m = (1.46 \pm 0.02) \times 10^{-3}$  M, determined according to the diffusion coefficient for components of reaction medium,  $D = 2.72 \times 10^{-22}$  m<sup>2</sup>/s, is practically agree with experimental constant for  $\alpha$ -chymotrypsin immobilized by phosphatidylcholine or phosphatidylinositol bilayer vesicles.

### 856.H3 UV-, CD- AND FLUORESCENT PROBE STUDY OF MICELLE STRUCTURE OF DNA COMPLEXES WITH CATIONIC AMPHIPHILIC MOLECULES

Boris I. Sukhorukov<sup>1</sup>, Ruben L. Kazaryan<sup>1</sup>, Alexander I. Petrov<sup>2</sup>, Gleb B. Sukhorukov<sup>1</sup>,  
Ludmila I. Shabarchina<sup>1</sup>, Michael M. Montrel<sup>1</sup>

<sup>1</sup>*Institute of Theoretical and Experimental Biophysics, Rus. Acad. Sci., Pushchino, Russia;*

<sup>2</sup>*Institute of Crystallography, Rus. Acad. Sci., Moscow, Russia.*

One of the new directions in colloid science is the study of the structure, properties and stability of the micelles containing nucleic acids. The interest to these systems is connected, first of all, with the solving

one of the important problems of modern biology and medicine: increasing the efficiency of transmembrane transport of nucleic acids. The probability of the transition of negatively charged and hydrophilic DNA through the negatively charged and hydrophobic biological membrane is very low. One of the ways to increase this probability lies in the formation of DNA complex with a surfactant, in particular, with cationic amphiphilic molecules. Here we present the results of comparative study of the structure, stability and optical properties of DNA complexes with aliphatic amines and their N-alkyl substituted derivatives. The information about the structure and spectral peculiarities of DNA complexes with these amphiphilic molecules which hydrocarbon chain length varying from C10 to C16 was obtained by UV- and CD-spectroscopy and luminescent probe pyrene. The UV-spectroscopic peculiarities are connected with earlier unknown dependence of hypochromic effect of DNA on concentration of micelle-like structures of complexes and peculiarities in CD-spectra with changes of DNA spatial structure. It was found that critical micelle concentration of these cationic amphiphiles is about one order lower in the presence of native or denatured DNA and practically does not depend on its conformational state. It was demonstrated that in solutions with definite ionic strength aliphatic amines may both stabilise and destabilise the DNA double helix. The result depends on the amine concentration. At low concentration of aliphatic amines, the amines interact with phosphate groups of DNA and decrease the electrostatic repulsion between negatively charged sugar-phosphate chains that results of the stabilisation of the doublehelix. Aliphatic amines being in high concentrations begin to interact with nucleic bases. This interaction results in the substitution of intramolecular base-base H-bonding by intermolecular base-amine H-bonding. Impossibility of such a substitution in the case of N-alkylsubstituted derivatives of aliphatic amines with long chain supports this conclusion. We have shown that DNA is unwound in micelles of its complexes with aliphatic amines but remains in double-helical state in micelles of its complexes with N-methylsubstituted derivatives of the aliphatic amines. These data are in good agreement with the results of studying of multilayer LB-films formed by DNA complexes with cationic amphiphiles. In LB-films of complexes with long chain aliphatic amines DNA is in fully unwound state, whereas in LB-films of complexes with N-alkylsubstituted derivatives of amines DNA preserve its double-helical structure [1,2].

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## 857.H3

### BACTERIAL MONOLAYERS AT MODEL FLUID INTERFACE

Vesna Svetlicic<sup>1</sup>, Nadica Ivosevic<sup>1</sup>, Vera Zutic<sup>1</sup>, R. A. Long<sup>2</sup>

<sup>1</sup>Center for Marine Research Zagreb, Rudjer Boskovic Institute Zagreb, Croatia

<sup>2</sup>Marine Biology Research Division, Scripps Institution of Oceanography,  
University of California, San Diego, La Jolla, California

In marine environment the interfaces with a high tendency of accumulating bacteria and biofilm formation are often fluid or flexible. We studied initial monolayer formation in seawater and 0.1 M NaCl solution using expanding mercury sphere electrode and marine bacteria that differ in their tendency to aggregate. The experiments were performed under conditions of maximum attraction at the positively charged and hydrophobic interface and enhanced transport to the interface by convective streaming. Time of contact between bacteria and the dropping mercury electrode (DME) is too short (2 seconds) for production and release of specific attachment mediators. Adhesion of bacteria at DME immersed directly in the cell suspension is manifested as an increase of fractional surface coverage in the range of cell densities from  $2 \times 10^5$  to  $5 \times 10^7$ /ml. By further increase in the cell density the electrochemical response reaches a form that reflects full coverage of the electrode with organic material that displaced counter ions and water molecules from the interface. Maximum surface cell density was estimated at  $5 \times 10^5$  cells/cm<sup>2</sup>. Rate of initial monolayer formation is transport controlled while adhesion of single cells is a faster process. In the case of aggregated cells the process of film formation is slower as the transport of an aggregate from the bulk to the interface is slower than of single cells. After attachment, aggregates undergo a slower (50-200 ms) transformation into a monolayer patch at the interface. We have identified prevailing hydrophobic over electrostatic interactions in the initial monolayer formation by adhesion of aggregated cells. Freshly exposed surfaces such as air bubbles, and air/water interface in general, as well as oil droplets are the closest analogues to our model.

**858.H3****FORMATION AND PROPERTIES OF NEW SURFACE-ACTIVE  
GELATIN DERIVATIVES****Ofer Toledano, Shlomo Magdassi***Casali Institute of Applied Chemistry, The Hebrew University of Jerusalem, 91904, Jerusalem, Israel*

Surface-active gelatin was formed by covalent attachment of hydrophobic chains to the gelatin molecule. The chemical modification was carried out by reacting N-hydroxy succinimide esters of various fatty acids ( $C_4$ - $C_{18}$ ), with the primary amino groups on the protein backbone, using DMSO as the solvent. Gelatin molecules were modified at high and low degrees of attachment and at 25°C and 45°C. The modified gelatin was found to have higher hydrophobicity and better surface activity than the native gelatin. The surface activity was evaluated by surface tension measurements, emulsification and adsorption on the oil-water interface. It was found that, in general, the modified gelatins are more surface-active with the increase in hydrophobic chain length and the number of attached chains per gelatin molecule. In addition, smaller emulsion droplets were obtained and the emulsions were stable when modified gelatin was used. The modified gelatins have also high foaming ability and a high foam stability. The surface-active gelatin was also compared to classical surfactants and was found to have similar surface activity at much lower concentration.

**859.H3****PROTEIN CRYSTALLIZATION -  
GROWTH AND NUCLEATION OF LYSOZYME CRYSTALS****D. Tsekova, S. Dimitrova, C. N. Naney***Institute of Physical Chemistry, Bulgarian Academy of Sciences*

The scientific interest in protein crystallization is increasing steadily (1) due to the believe that more light can be shed on important problems in molecular biology and live sciences. Some very complex protein/protein interactions can be tackled basing oneself on the exact knowledge of the interactions in protein crystals at the molecular level. Atomic resolution crystal structures are needed to establish the structure to biological function relationships and hence, also to design drugs. Big and highly perfect protein crystals are indispensable for this purpose. A profound knowledge of all the peculiarities of the crystal growth process is the prerequisite for their preparation. Several sophisticated techniques, like atomic-force microscopy, Michelson laser interferometry, etc., have been used to investigate thoroughly the crystal growth on a molecular level. But even more simple approaches, namely careful morphological studies, can still provide valuable information on some peculiarities of protein crystals, since the morphology is a very important characteristic of every crystal. For instance, the good polygonized shape is an important prerequisite for crystal perfection. On the contrary, gross morphological defects are always connected with other crystal imperfections (2).

The main source of our information is the careful investigation of the preferred orientation of HEWL (hen-egg-white lysozyme) crystals on glass supports. A modification of the well-known double-pulse technique has been used, applying thermal "pulses". In order to distinguish between homogeneous and heterogeneous nucleation, as well as take into consideration gravity effects, cooling (by Peltier-elements) was performed in two different ways - from the top and from the bottom of the two-dimensional cells. Differently oriented crystals were observed depending on the growth conditions. Besides, it was found that like to the crystals built by small molecules, HEWL crystals exhibit polyhedral instability when grown under diffusion limitations.

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**860.H3****WETTABILITY AND ADHESION OF MARINE AND RELATED  
ADHESIVE PROTEINS****Hiroyuki Yamamoto, Ayako Nishida and Kousaku Ohkawa***Institute of High Polymer Research, Faculty of Textile Science and Technology,  
Shinshu University, Ueda-city, 386 Japan*

Nature's powerful adhesives, secreted by marine mollusks such as mussels and barnacles, which must routinely cope with the force of surf and tides, are simple proteins. The proteins are designated as 'marine adhesive proteins' and their adhesive properties have been investigated with regard to their use as adhesives for biotechnological purposes. The primary structure of adhesive proteins of blue mussel *Mytilus edulis* was first determined by Waite to be (Ala-Lys-Pro-Ser-Tyr-Hyp-Hyp-Thr-Dopa-Lys)<sub>n</sub> and this protein was chemically synthesized by us. Later, some of marine adhesive proteins have been identified as Tyr/Dopa containing proteins which are also rich in Lys and Gly. Among many research approaches for marine adhesive proteins, however, characteristics of biological adhesion have not been examined from the standpoint of molecular structures such as amino acid species and their sequences. In order to evaluate the role of individual amino acids together with the sequences in marine adhesive proteins, in the present symposium the wettability, adhesion and adsorption characteristics of marine adhesive proteins in aqueous conditions, together with natural pearl oyster adhesive proteins and chitosan, on solid surfaces have been investigated by the following approaches at (a) the air-liquid interface (contact angles, surface free energies, and works of adhesion) and at (b) the liquid-solid interface (total surface free energies, together with the divided dispersion and polar components, and work of adsorption). When the total surface free energies were divided into the dispersion and polar components, the dispersion components exhibited an almost constant value of about 26-28 mJ/m<sup>2</sup> but the polar components changed from 3 to 14 mJ/m<sup>2</sup>. Thus, the total surface free energies were affected by the polar component of polypeptides and bivalve proteins. The work of adsorption of adhesive proteins exhibited higher values (41-68 mJ/m<sup>2</sup>) on teflon and polyethylene and the lowest values (6.9 mJ/m<sup>2</sup>) on glass. In addition, when one immerses a solid substrate in sea water, polysaccharide first adsorbs the substrate surface and the protein adsorption follows. In fact, biological adhesion in nature occurs in this order.

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**861.H4****INFLUENCE OF SURFACE POLYMER DENSITIES ON  
BIODISTRIBUTION OF SMALL (<30 nm) IRON OXIDE NANOPARTICLES****Babes L., Denizot B., Tanguy G., Le Jeune J.J., Jallet P.***Laboratoire de Biophysique, Faculté de Médecine, 1 rue Haute de Reculée, 49045 Angers Cedex, France*

The biodistribution of polymer coated hundred-nanometer scaled nanoparticles is greatly influenced by the hydrodynamic size, surface charge and polymer densities. In fact, adsorption of plasma proteins such as albumin and activation of the complement system are the limiting factors of vascular remanence. Because of the small size of our iron oxide nanoparticles used as MRI superparamagnetic contrast agent, we have characterized dynamic biodistributions as a function of the length and surface density of dextran polymeric coating as well as the complement system activation.

The 4.3 nm iron oxide cores, doubly labelled by radioactive <sup>59</sup>Fe and <sup>99m</sup>Tc, were coated by polymeric dextran (10 or 40 KDa) at surface densities ranging from 23 to 650 molecules per particle (0.41 to 11.4 molecule/nm<sup>2</sup>) and from 17 to 89 molecules per particles (0.29 to 1.56 molecules/nm<sup>2</sup>) respectively, and injected IV in rats. Scintigraphic Tc pharmacokinetics were compared with Fe post-mortem distribution. Activation of the complement system was assessed for human and rat sera by the CH50 method.

Hydrodynamic radii vary with the length of the polymer and the density, light scattering measurements roughly according with the theoretical model of De Gennes. Low density coatings induce greater complement activation and lower vascular residence times. Higher density coatings allow hydrodynamic radii of ≈16 nm and ≈26 nm, and ≈16 and 45 min of intravascular half-lives, for 10 and 40

kDa dextran coatings, respectively. Kinetics of liver and spleen captures depend on the type of particles and their coating densities.

The interfacial density is too important to allow polymeric mushroom isolation. Furthermore, contrarily to polymer bearing liposomes, these nanoparticles can be considered as very highly curved. Then, the complement activation would be due to the relative immobility of the polymeric chains rather than to the visibility of the iron oxide cores.

## 862.H4

### PROTEIN-MEDIATED FLUORIDATION AND ENAMEL DEMINERALIZATION AN IN VITRO APPROACH

E.S. Boteva<sup>1</sup>, A.J. Rugg-Gunn<sup>2</sup>, S.M. Higham<sup>3</sup>, E.I. Dulgerova<sup>1</sup>

<sup>1</sup>*Department of Conservative Dentistry, Faculty of Stomatology, Sofia, Bulgaria*

<sup>2</sup>*Department of Child Dental Health, Dental School, Newcastle University, UK*

<sup>3</sup>*Oral Biology Unit, School of Dentistry, Liverpool University, UK*

The aim of the present study was to compare the level of remineralization of demineralized enamel, after treatment with fluoridated milk, fluoridated water and ordinary milk in vitro. Twenty fully mineralized permanent human teeth with natural white spot precavitated lesions were sectioned (n=120). These were polished down to give a planoparallel section of 90 (+10) microns thickness. All specimens with defects were discarded. Eighteen satisfactory sections, twelve of which had natural white spot precavitated lesions and six with artificially produced (on sound enamel) lesions, were randomly allocated into the 3 groups. They were cycled in their respective solutions for 10 days: (a) 5 ppm whole full cream fluoridated milk, (b) 5 ppm fluoridated water and (c) ordinary whole, full cream milk. The sections, partly covered with varnish, were placed in baskets and immersed into the solutions twice each day for two hours and into CMC artificial saliva Glandosane (pH 7.2) twice each day for two hours, incubated at 37°C, and stored overnight in a fridge (4°C). Baseline and post treatment parameters were obtained for each specimen using polarised light microscopy and microradiography: (mA 10, kv 25, T 20 min). A higher level of remineralization was found in the fluoridated milk group (R=27%) compared with fluoridated water (R=8%) and ordinary milk (R=6%). Results from the polarised light microscopy were consistent with these findings. The milk-Fluoride hydrocolloidal system is a possible active component on the surface of the demineralized enamel, which takes part in the protein-mediated remineralization.

## 863.H4

### EFFECT OF THE PH ON THE STABILITY OF AN AMPHIPHILIC DRUG MONOLAYER

Y. Bouligand<sup>1</sup>, F. Boury<sup>2</sup>, J.M. Devoiselle<sup>3</sup>, J.C. Gautier<sup>4</sup>, J.E. Proust<sup>2</sup>, P. Saulnier<sup>2</sup>

<sup>1</sup>*Laboratoire d'Histophysique, EPHE, Angers, France*

<sup>2</sup>*Laboratoire de Biophysique Pharmaceutique, Faculty of Pharmacy, Angers, France*

<sup>3</sup>*Faculty of Pharmacy, Montpellier, France*

<sup>4</sup>*Sanofi Recherche, Montpellier, France*

Amiodarone hydrochloride, because of its antianginal and antiarrhythmic properties is a drug widely used in the treatment of heart diseases. Because of its poor solubility in water, the solubilization of amiodarone is performed by heating above 60°C the amiodarone powder prealably suspended in an aqueous media. In this way it is possible to obtain perfectly transparent and limpid preparations (at concentration above 50 mg/ml) which remain stable at ambient temperature. Microscopy light scattering and photon correlation spectroscopy studies have strongly suggested that the isotropic liquid phase obtained in water consisted probably in an inverse and water rich sponge phase made from cylindrical and branched micelles (1). However, by dilution under 2 mg/ml, a large instability is observed and turbidity appears.

In order to overcome formulation problems and to produce a preparation, stable at high concentration which remains stable on dilution without use of large quantities of stabilizing agent, a better understanding of physico-chemical parameters appears necessary. The influence of pH, ionic strength, and the nature of the dissolved salts on the self assembly properties of the amiodarone molecules and their supramolecular organization was investigated. Experimentally, amiodarone monolayers were spread at the



air/water interface from organic or aqueous preparation and the effects of pH or presence of counterions in the aqueous phase supporting the monolayer were analysed. The stability of the monolayers spread from organic solutions is strongly pH dependent and total desorption of the molecules occurs at acidic pH (HCl, pH 4.4), while a good stability is observed at basic pH. On buffered subphases ( $\text{Na}_2\text{HPO}_4$ , pH 4.4) the monolayer becomes stable but a plateau with abnormally high surface pressures (2 mN/m) is observed for high molecular areas (400-80  $\text{\AA}^2/\text{molecule}$ ). AFM images of the sampled monolayer have shown the formation of a continuous network with microholes a few  $\text{\AA}$  deep. This transition reflects macromolecular associations probably involved in the liquid crystalline phase forming the stable volumic phases. Similar interfacial behavior and patterns are observed when spreading the aqueous preparations (sponge phase) on subphases with moderate or acidic pH. However, large instabilities occur at basic pH indicating the breaking of the sponge phase into soluble vesicles during the spreading.

These results are discussed by involving the pH dependent charge of the amiodarone molecule and the electrostatic interactions between molecules and counterions.

#### 864.H4 DYNAMIC BEHAVIOR OF SURFACE FILMS FROM EXOGENOUS SURFACTANTS (CUROSURF<sup>TM</sup>, EXOSURF<sup>TM</sup>) AND NEWBORN TRACHEAL ASPIRATES DURING CLINICAL TREATMENT

Y. Christova<sup>1</sup>, R. Todorov<sup>1</sup>, E. Enchev<sup>1</sup>, E. Christova<sup>2</sup>, Z. Lalchev<sup>1</sup>

<sup>1</sup>Dept. of Biochemistry, Faculty of Biology, Sofia University, 8 Dragan Tzankov Blvd., 1421 Sofia, Bulgaria;

<sup>2</sup>Department of Pediatrics, Medical Faculty, Medical University, Sofia, Bulgaria

Alveolar surfactant (AS) is a thin liquid film containing lipids and specific proteins, which lines the alveolar surface and lowers surface tension to prevent collapse at end-expiration. The insufficiency of AS causes respiratory distress syndrome (RDS), the main reason for the morbidity and mortality in premature newborns. The most perspective therapy of RDS is the treatment with exogenous surfactants EXOSURF<sup>TM</sup> (Burroughs Wellcome Co., Research Triangle Park, NC) and CUROSURF<sup>TM</sup> (Chiesi Farmaceutics SpA, Parma, Italy).

Dynamic characteristics of monolayers from the exogenous surfactants were studied by Wilhelmy surface balance. Maximum and minimum surface tensions ( $\gamma_{\text{max}}$  and  $\gamma_{\text{min}}$ ) and the hysteresis curves during compression-decompression were measured. Better spreading within the first 10 seconds were observed for EXOSURF, but the monolayers from CUROSURF reached lower equilibrium  $\gamma_{\text{max}}$  value. Lower value of  $\gamma_{\text{min}}$  and much better respreading during decompression were measured for CUROSURF monolayers. We consider these differences to be due to the presence of the hydrophobic surfactant proteins SP-B and SP-C in CUROSURF.

Surface activity of monolayers of tracheal aspirates (TA) from newborns with RDS before and after treatment with CUROSURF and EXOSURF were investigated. The results were compared with the total phospholipid content (TPL) of the samples. It was shown better spreading and surface activity of the films from TA after treatment compared to those before treatment. A great improvement of spreading and dynamic surface characteristics of monolayers from TA after treatment with CUROSURF were observed. It was shown a good correlation between  $\gamma_{\text{max}}$  and  $\gamma_{\text{min}}$  values of the TA films and the TPL content of the TA samples.

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#### 865.H4 BLACK FOAM FILM FROM ALVEOLAR SURFACTANT FORMATION AND STABILITY

Dotchi Exerowa<sup>1</sup>, Zdravko Lalchev<sup>2</sup>

<sup>1</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

<sup>2</sup>Dept. of Biochemistry, Faculty of Biology, Sofia University, 8 Dragan Tzankov Str., Sofia 1421, Bulgaria

A new approach to the study of the lung surfactant system is considered. An *in vitro* model - microscopic foam films is introduced. Black foam films from alveolar surfactant, amniotic fluid in various



gestation weeks as well as individual phospholipids are investigated under conditions (size, capillary pressure etc.), close to those in the alveoli. Parameters characterizing the formation and stability of these black foam films, i.e. threshold concentration for the formation of a stable film, the binding energy of the phospholipid molecules in the foam bilayer etc., are introduced and evaluated. All the results obtained with thick films (long range molecular interactions) and black foam films (short-range molecular interactions) indicate that normal interactions play a significant role in the stability of foam bilayers from both alveolar surfactants and amniotic fluids. These studies are in very good agreement with the biomedical ones and give new trends in the study of lung surfactant lipid-protein interactions.

## 866.H4 METHOD FOR ASSESSMENT OF FETAL LUNG MATURITY: NEW RESULTS

Dotchi Exerowa<sup>1</sup> and Zdravko Lalchev<sup>2</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Science, Sofia 1113, Bulgaria*

<sup>2</sup>*Dept. of Biochemistry, Faculty of Biology, Sofia University, 8 Dragan Tzankov Str., Sofia 1421, Bulgaria*

The "black film method" for the assessment of fetal lung maturity is based on the possibility for spontaneous formation of a stable, with respect to rupture, black foam film obtained from any samples consisting of the major components of lung surfactants, e.g. amniotic fluids (AF). The method is constructed to reflect the spontaneous molecular interactions, taking place at the air/liquid interface, the same which lines the alveolus. Thus, at one especially chosen dilution of the samples under examination, say reference value of dilution (RVD), mature LS samples give stable black films but the films from immature samples are not stable and invariably rupture under the same conditions. The choice of optimal RVD that reveal the highest potential "to recognize" mature from immature samples, is statistically dependent. In the case of using AF in order to estimate the risk for RDS development after delivery, TD have to be involved from comparison between the test results (yes or no of black film) and clinical outcome (yes or no of RDS) of sufficiently enough newborns. Our previous results, based on 182 AF samples showed the value of RVD is between 3.2 -3.4. Based on the statistics from 817 cases, we now report that at RVD=2.8 all AF samples which did not develop RDS gave black films. 150 from 162 AF samples which developed RDS did not form black films but 12 were able to form. The prognostic potential of intermediate RVDs between 2.0 and 2.7 is discussed.

## 867.H4 INFLUENCE OF LUNG SURFACTANT PROTEINS (SP-A, SP-B) FOR THE DYNAMIC PROPERTIES OF SURFACE FILMS OF CLINICAL SURFACTANT PREPARATIONS (ALEC<sup>TM</sup>, EXOSURF<sup>TM</sup>)

Alan Mackie,<sup>1</sup> Yonka Christova,<sup>2</sup> Shab Ladha,<sup>1</sup> Zdravko Lalchev<sup>2</sup>

<sup>1</sup>*Food Biophysics Department, Institute of Food Research, Norwich Laboratory, Norwich Research Park, Colney, Norwich NR4 7UA, England*

<sup>2</sup>*Dept. of Biochemistry, Faculty of Biology, Sofia University, 8 Dragan Tzankov Str., 1421 Sofia, Bulgaria*

Rate of spreading, surface tension lowering capacity and film behavior at the air/liquid interface during compression-decompression in a Langmuir surface balance of spread suspensions from commercial preparations used for surfactant replacement therapy of RDS (respiratory distress syndrome) were studied. It is known from the clinical practice that the synthetic, protein-free preparations ALEC<sup>TM</sup> (Britannia Pharmaceuticals Ltd) and EXOSURF<sup>TM</sup> (Burroughs Wellcome Co., Research Triangle Park, NC) given to very premature babies at birth significantly reduce their mortality, the incidence of pneumothoraces and reveal a beneficial effects regarding the respiratory support needed. The *in vitro* surface activity of ALEC (composed of dipalmitoylphosphatidylcholines and phosphatidylglycerols, DPPC:PG=7:3 w/w) and EXOSURF (composed of DPPC:Tyloxapol:Hexadecanol=84:7:9 w/w) and the effect of Tyloxapol and Hexadecanol upon it were investigated. It was found that, at initial equal surface concentration, the EXOSURF sample showed a higher rate of spreading and much higher surface pressure of the film at the end-point of compression than ALEC. The films of ALEC showed better spreading and maximum surface pressure when it was spread in "dry" state.

The role of surfactant proteins isolated from porcine lungs and added to the EXOSURF and ALEC samples was in particular studied. It was shown that both the hydrophilic SP-A and hydrophobic SP-B proteins enhance the rate of spreading and surface activity at the air/liquid interface of the preparations. In addition, the mixtures with SP-B showed a more significant increase in surface activity (in term of surface pressure during compression) and film elastic modulus than those with SP-A. The results are discussed in the light of the presence in ALEC of negatively charge PG which could interact with proteins, resulting in formation of a more soluble lipid-protein complex.

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## 868.H4

### VOLUME BEHAVIOR ON THE MIXED MICELLIZATION OF CATIONIC SURFACTANT AND LOCAL ANESTHETICS

Hitoshi Matsuki<sup>1</sup>, Michio Yamanaka<sup>2</sup>, and Shoji Kaneshina<sup>1</sup>

<sup>1</sup>Department of Biological Science and Technology, Faculty of Engineering,  
The University of Tokushima, Minamijosanjima, Tokushima 770, Japan

<sup>2</sup>Department of Chemistry, Faculty of Science, Kyushu University Ropponmatsu,  
Ropponmatsu, Fukuoka 810, Japan

The volume behavior of two local anesthetics, tetracaine hydrochloride (TC•HCl) and procaine hydrochloride (PC•HCl), incorporated into micelles formed by decylammonium chloride (DeAC) was investigated by measuring the densities of aqueous solutions of DeAC-TC•HCl mixture and DeAC-PC•HCl mixture. By analysing the experimental data thermodynamically, the DeAC and TC-HCl molecules in the monomeric and micellar states were found to mix ideally from the view point of volume. On the other hand, it was proved in the case of DeAC-PC•HCl system that the volumes of DeAC and PC•HCl molecules behave ideally in the monomeric state, while the PC•HCl molecules do not contribute to the volume of micelle formation for DeAC and they are not incorporated into DeAC micelles at all. Further, the compositions of local anesthetic in the micelle, which were obtained from the composition dependence of critical micelle concentration, clearly said that the TC•HCl molecules are considerably incorporated into DeAC micelle whereas the PC•HCl molecules conversely are expelled from the micelle. The results are correlated with the local anesthetic potency of TC•HCl and PC•HCl, and correspond to those obtained from the volume of micelle formation.

## 869.H4

### PHASE STATES OF FOAM BILAYERS FROM NATURAL AND SYNTHETIC LIPID-PROTEIN MIXTURES

A. Nikolova<sup>1</sup>, Z. Lalchev<sup>2</sup>, R. Todorov<sup>2</sup> and D. Exerowa<sup>1</sup>

<sup>1</sup>Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

<sup>2</sup>Department of Biochemistry, Faculty of Biology, Sofia University, Sofia 1421, Bulgaria

The phase states of the thinnest black foam films formed from natural (human amniotic fluid and porcine lung surfactant) and synthetic (Infasurf) lipid-protein mixtures were studied by the thin liquid film microinterferometric technique of Scheludko and Exerowa. The temperature dependence of the critical concentration  $C_c$  for formation of black foam film was obtained for the lipid-protein mixtures studied. This concentration was detected from the experimental dependence of the probability for observation of black foam film in common foam film on the bulk amphiphile concentration. The experimentally determined temperature dependence of  $C_c$  is linear in Arrhenius co-ordinates. The binding energy  $Q$  of an amphiphile molecule in the black foam film was estimated from the  $\ln C_c(1/T)$  dependence according to the hole-nucleation theory of Kashchiev and Exerowa for the stability and permeability of bilayers. The value of  $Q$  is about  $16kT$  for the black foam films formed from the three lipid-protein mixtures studied. This value coincides with the one obtained for liquid crystalline foam bilayers from dipalmitoylphosphatidylcholine. This coincidence is an evidence that the black foam films studied do not undergo phase transitions and are in the liquid crystalline state at the temperatures which are of importance for the physiological processes and

that phosphatidylcholines are of major significance for the formation and stability of black foam films from amniotic fluid, lung surfactant and Infasurf.

## 870.H4

### INTERMOLECULAR INTERACTIONS IN COLLOIDS AT CREATION OF LONG ACTION DRUGS

V.V. Rodin<sup>1</sup>, V.N. Izmailova<sup>2</sup>, V.I. Gaitan<sup>3</sup>, A.V. Kharenko<sup>4</sup>, K.V. Alekseev<sup>4</sup>

<sup>1</sup>*Institute of Physical Chemistry (RAS), Moscow, Russia*

<sup>2</sup>*Moscow State University, Moscow, Russia*

<sup>3</sup>*State Research Centre for Applied Microbiology Moscow region, Russia*

<sup>4</sup>*SIA "Biotechnologia", Moscow, Russia*

**Introduction.** The speed of drug release is often regulated by the state of interpolymer complexes (IPC) that are used as polymer carriers [1-3]. The work presents the structural, colloidal and dynamical characteristics of IPC or carriers from one polymer concerning different states: solution, gel and solid. The study examines the interactions between components of long action drugs which are tested by different NMP, approaches at IPC-construction as well as at release of biomolecules.

**Experimental:** Polyacrylic acid (PAA), rarely-linked polyacrylic acid (RL/PAA), polymethacrylic acid (PMAA), polyethylene glycol (PEG), polyvinylpyrrolidone (PVP). IPC PMAA-PEG, PAA-PEG, RL/PAA-PVP were made by different ways [2]. Aminazinum ( $H^+Am$ ) was used in reactions of competition with PEG-molecules. <sup>13</sup>C- CP/MAS NMR-spectra were made on MSL-300 (Bruker) spectrometer. NMR-experiments of liquid samples were carried out with the AMX-400 spectrometer (Bruker). NMR-relaxation data were obtained by SXP-100 (90 MHz) NMR-spectrometer (Bruker). The diffusion coefficients (D) were obtained by method of PGSE (pulsed-gradient-spin-echo).

**Results.** It was observed that IPC as carriers of drugs had some different kinetic parameters [2,3]. IPC of mixing construction way was characterized by high level of drug release. A model of drug outflow [2] was used to explain the NMR-results. Two ranges with different pH-dependence of IPC- $H^+Am$  composition [ $Z=[H^+Am]/[IPC]$ ] were obtained. Present study shows the triple PMAA-PEG- $H^+Am$  complex involves the electrostatic interactions between  $H^+Am$  and carboxylic groups that are situated in the IPC-defects ( $Z \leq 0.2$ ). In the range of  $Z \geq 0.2$  IPC is dissolved and large  $H^+Am$ -amount is involved into the composition.  $T_2$  and D-data were obtained for RL/PAA -water system with additives in gel state preparations. The decrease of D-value was compared for water and additives.

**Conclusion.** The results testified the role of IPC-relaxation processes in molecular dynamics of long action drugs. The IPC from matrix polymerization had more structural order than the one from mixing construction way. IPC-drug system at different conditions obtained properties of macromolecules and biosubstance during the change of the state from solid to gel and solution. A reaction scheme between IPC and aminazinum was proposed. The release of PEG macromolecules with the aid of  $H^+Am$  is owing to the competition.

1. Rodin V.V. et al. [1994] *Kolloidnyi Zh.* 56: 84-90.

2. Rodin V.V. et al. [1996] *Kolloidnyi Zh.* 58: 671-679.

3. Rodin V.V., Izmailova V.N. [1996] 13th ESMRMB Meeting :Abstracts. Prague. P. 251.

## 871.H4

### THE SURFACE OF MAMMALIAN PULMONARY ALVEOLI IS A FOAM NETWORK

Emile M. Scarpelli

*Perinatology Center, Cornell University, College of Medicine, NY, USA*

The pulmonary acinus is a branching system of alveolar ducts formed by a contiguous agglomerate of histologically discrete, gas-containing pockets (alveoli) that have been described as forming in dodecahedral or tetrakaidecahedral clusters. The continuous thin liquid surface that covers the alveolar epithelial cells is the repository of pulmonary surfactants secreted by the type 2 pneumocyte of this cellular monolayer. Recent discoveries (1978-1983) reveal that the thin liquid surface is in fact a foam network of

bubble films in which each alveolar bubble apposes adjoining alveolar and ductal bubbles. Liquid circulating within the network is channeled through conduits formed by the molecular bilayer films of the bubbles. The network is established during the first postnatal hour of life and persists - as a reciprocating and renewable entity - throughout life. (In contrast, the conducting airways from trachea through pre-acinar bronchioles remain bubble-free in the normal lung). The following characteristics of the foam network have been established: (1) Pulmonary surfactant deficiency (e.g., immature lungs) or blockade (e.g., by antifoams) disallow formation and result in respiratory failure. (2) The bubble film is the fundamental infrastructure of the alveolus; its removal results in immediate collapse (airlessness) of the unit. (3) In situ, bubble films are expanded during inflation and compressed during deflation without loss of film integrity. (4) With time and particularly at low lung volumes, bubble size is reduced (e.g., to <30  $\mu\text{m}$  diameter), the unit destabilizes, film surfactants are re-dispersed in the liquid layer, and the bubble collapses. (5) Re-inflation results in new bubble formation at the site. (6) In the laboratory, the network can be dried and re-hydrated reversibly without loss of film integrity. (7) Air-liquid surface tension is near zero. (8) Respiratory gases diffuse rapidly through the films. Whereas bubbles in normal lung parenchyma in vivo (the alveolar foam network) were discovered by direct observation through the stereomicroscope, their presence and significance had been unrecognized previously. There are three principal reasons for this failure. First is the difficult resolution of tissue and bubble film surfaces in fresh lung tissue. This was resolved by adopting visual perspectives that permit identification of bubble films by micromanipulation and microsurgery. Second: Often all gas was removed from the lungs ("degassing") prior to study. The invalidity of this procedure was revealed by the demonstration that forced disruption of bubbles during degassing is always followed by bubble/network re-formation when the lungs are re-inflated. Third, the vast majority of alveolar studies required fixation, chemical dehydration, embedding, and sectioning of the tissue prior to microscopic examination. This was resolved by development of a method of "agar pre-embedding" in which agar forms a protective mantle over the films and intact bubbles in the network and thus permits subsequent histological processing and examination by light and electron microscopy. Further characterization of the alveolar foam network includes the following areas integral to normal lung function. (1) Fluid dynamics of bubble formation and network assembly. (2) Vital interactions between network forces ("Plateau dynamics") and tissue forces (viscoelasticity; hydrostatic and oncotic pressures). (3) Formation and stability of the thin liquid films and "Exerowa surfactant black films" that may define the network itself.

## 872.H4 DRAINAGE OF MICROSCOPIC FOAM FILMS FROM INFASURF

R. Sedev<sup>1</sup>, N. Antonova<sup>2</sup>, Ya. Ivanov<sup>3</sup> and D. Exerowa<sup>1</sup>

<sup>1</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>2</sup>*Institute of Mechanics and Biomechanics, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

<sup>3</sup>*Central Laboratory of Physico-Chemical Mechanics, Bulgarian Academy of Sciences, Sofia 1113, Bulgaria*

Recently foam film formation from therapeutic surfactants was studied [1]. The morphology and stability were emphasized. Among the three preparations tested INFASURF was found the most effective. In this study we report in more details the thinning behavior of foam films from INFASURF.

The foam film drainage has been carried out in a Scheludko-Exerowa cell. The time,  $\tau$ , from initial film formation to the first black spot appearance has been recorded at capillary pressure  $P_C = 400, 1200$ , and  $2400 \text{ dyn/cm}^2$ . All experiments were done with fresh aqueous solutions at  $37^\circ\text{C}$ .

It is assumed that the drainage of foam films is described with Reynolds equation. Then

$$\tau = \int_0^r dt \equiv \frac{r^2}{h_{CR}^2} \frac{\eta}{P_C}$$

where  $\eta$  is the bulk viscosity,  $r$  the film radius ( $\sim 100 \mu\text{m}$ ), and  $h_{CR}$  the black spot thickness ( $\sim 30 \text{ nm}$ ).

It is found that  $\tau$  linearly increases with  $1/P_C$  in agreement with the above equation. Since  $r$  and  $h_{CR}$  are constant the slope of this linear dependence is directly proportional to  $\eta$ . Thus viscosity can be monitored with film thinning experiments.

The effect of electrolyte concentration is significant. Drainage is faster when electrolyte is added. No practical difference between  $0.14 \text{ M}$  and  $0.5 \text{ M}$   $\text{NaCl}$  is found. The INFASURF concentration was varied from  $100$  to  $550 \mu\text{g/mL}$ . The viscosity initially increases and then levels off at a plateau value.

The bulk viscosity has been monitored under steady flow conditions with a LS 30 Sinus Contraves viscometer. Measurements at shear rates from 0.02 to 130 s<sup>-1</sup> showed that INFASURF solutions have Newtonian behavior. Therefore they can be characterized by a single value of the viscosity.

There is reasonable agreement between the viscosity values from bulk and film measurements.

1. E.M. Scarpelli, A.J. Mautone, Z. Lalchev, and D. Exerowa (1996) Colloids & Surfaces B (in press)

## 873.H4 PEG-COATED BIOMEDICAL SURFACES STUDIED FOR THEIR INTERACTION WITH LIVING CELLS

T. Vladkova<sup>1</sup>, M. Malmsten<sup>2</sup>, N. Krasteva<sup>3</sup>, A. Kostadinova<sup>3</sup> and G. Altankov<sup>3</sup>

<sup>1</sup>University of Chemical Technology and Metallurgy, 1756 Sofia, Bulgaria

<sup>2</sup>Institute for Surface Chemistry 11486 Stockholm, Sweden

<sup>3</sup>Institute of Biophysics Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Cell-biomaterial interaction is of great importance for the development of biocompatible as well as hybrid surfaces. This study represents our initial results on the investigation of human foreskin fibroblasts interaction with PEG-coated surfaces differing on the length of the oxyethylene chain. PEG has been grafted to silica plates using branched poly(ethylene imine) (PEI) as an anchoring polymer.

To study the interaction with the living cells human fibroblasts were plated on the above described surfaces and studied by immunofluorescence with respect to the evaluation of the overall cell morphology, the organization of the actin cytoskeleton and the  $\beta_1$  integrin (major fibronectin receptor) distribution. The particular effect of fibronectin preadsorption (the major cell adhesive protein in the blood) to these materials have been studied. The results of living cells interaction have also been compared to the results of other proteins adsorption.

## 874.H4 AN ISOTHERMAL TITRATION CALORIMETRIC STUDY ON CHLOROFORM BINDING TO BOVINE SERUM ALBUMIN

M. Yamanaka<sup>1</sup> and I. Ueda<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Kyushu University Ropponmatsu, 4-2-1 Ropponmatsu, Chuo-ku, Fukuoka 810, Japan

<sup>2</sup>Department of Anesthesia, Department of Veterans Administration Medical Center, and University of Utah School of Medicine, Anesthesia 112A, DVA Medical Center, Salt Lake City, UT 84148, USA..

The binding of chloroform to bovine serum albumin (BSA) was studied by isothermal titration calorimetry. Because this method does not require to separate bound and free ligands in order to obtain binding parameters, it is particularly useful for examining the binding mode of highly volatile ligands such as chloroform. Isothermal titration calorimetric profiles were measured by titrating BSA solutions with chloroform solutions at 25 °C. From these profiles, the difference in enthalpy between the solutions with or without chloroform per mole of BSA,  $h^{dif}$  was estimated. The average partial molar enthalpy change of the complex formation per chloroform molecule,  $\Delta h$ , was determined on the basis of only the initial part of the  $\Delta h$  vs. the molar ratio of total chloroform molecules to total BSA molecules curve. The value of  $\Delta h$  was  $-10.37 \pm 0.29$  kJmol<sup>-1</sup>. Further, the average number of chloroform molecules bound to a BSA molecule,  $b$ , and the free chloroform concentration,  $C_x$ , were obtained. Using these values, the binding isotherms were constructed (Fig. 1). It was found that the binding was saturable and characterized by the Langmuir adsorption isotherms. In order to estimate the association constants,  $K_A$ , and the maximum binding number,  $B_{max}$ , of chloroform to

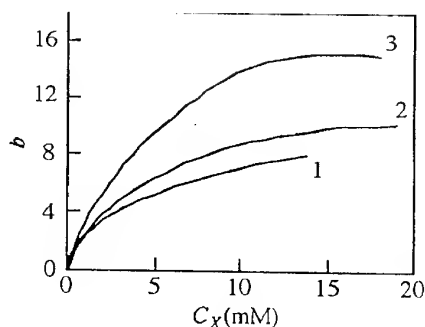


Fig. 1. The binding isotherms of chloroform to BSA at 25 °C. BSA concentrations are 1: 0.998, 2: 0.101, and 3: 0.0105 mM.

BSA, the  $b/C_x$  values were plotted against  $b$  (the Scatchard plots). The Scatchard plots were found to be nonlinear, which indicates the presence of multiple classes of binding. Because of the difficulty in identifying numerous intermediate classes of binding, the high- and low-affinity binding classes were analyzed. The results showed that the high-affinity  $K_A$  was  $2,150 \pm 132 \text{ M}^{-1}$  ( $K_D = 0.47 \text{ mM}$ ) with a  $B_{\max}$  of  $3.7 \pm 0.2$  and the low-affinity  $K_A$  was  $189 \pm 3.8 \text{ M}^{-1}$  ( $K_D = 5.29 \text{ mM}$ ) with a  $B_{\max}$  of  $13.2 \pm 0.3$ .

## 875.H5 MODIFICATION OF POLYMER SURFACE BY ADSORPTION OF BLOCK COPOLYMERS

Balin Balinov<sup>1</sup>, Jordan Petrov<sup>2</sup>, Rolf Myrvold<sup>3</sup>

<sup>1</sup>Nycomed Imaging, Oslo, Norway

<sup>2</sup>Institute of Biophysics, Bulgarian Academy of Sciences, Sofia, Bulgaria

<sup>3</sup>Department of Chemistry, University of Oslo, Norway

Wetting of a model substrate from a biodegradable polymer was characterised by advancing contact angles with various solutions of block copolymers. The hydrophilisation of the surface was quantitatively determined by a decrease of the free energy at the solid-liquid interface evaluated by the simultaneous measurement of the interfacial tension and the advanced contact angle. PEG-based block copolymers were studied as Pluronic F38, Pluronic F68, Pluronic F88, Pluronic F108 and the maximum decrease of the interfacial free energy were found at various polymer concentrations.

The state of the block copolymer in an adsorption layer is modelled by a monolayer of the block copolymer at the air-water interface as the surface pressure isotherm is measured by a Langmuir balance. Various known equations of states were tested to describe the effect of the molecular weight of the block copolymer at the constant length of PEG chain.

The approach is useful for a selection of a proper block copolymer for the required hydrophilisation of the polymer surface.

## 876.H5 PREPARATION OF ENZYME-HOSTED NANOPARTICLES THROUGH REVERSE MICROEMULSION

Tapas K. De, Manjari Lal and Amarnath Maitra

Department of Chemistry, University of Delhi, Delhi- 110 007, India

Extremely fine aluminium hydroxide nanoparticles containing peroxidase has been prepared using aqueous core of reverse microemulsion as nanoreactor (1 -10 nm size). The kinetic studies of the enzyme entrapped into these particles have been carried out at different pH and temperature in buffer. The activity of this entrapped enzyme prepared through reversed microemulsion of different water pool size and their temperature dependent stability have also been investigated. It has been observed that the aluminium hydroxide entrapped enzyme exhibits same trend of activity as that of free enzyme when dissolved in reverse micelles. However, the activity and shelf-life of the entrapped enzyme is higher compare to that of free enzyme. It is concluded that the active conformation assumed by the free enzyme in the aqueous core of the reverse micellar droplets is practically 'frozen' by the precipitated aluminium hydroxide gels under the same micellar conditions. An antigen derived from pathogenic fungus *aspergillus fumigatus*, entrapped in aluminium hydroxide nanoparticle has been found to produce antibody IgG in mice for a longer period compare to that due to free antigen mixed with aluminium hydroxide gel as an adjuvant. It shows prolong 'sustain release effect' when protein is entrapped into aluminium hydroxide nanoparticle.

**877.H5****THIN LIQUID FILMS FROM DISPERSIONS OF CELLULOSE ACETHOPHTHALATE WITH OPHTHALMIC DRUGS****E. Dimitrova<sup>1</sup>, M. Kaisheva<sup>2</sup>, D. Platikanov<sup>2</sup> and E. Minkov<sup>1</sup>**<sup>1</sup>*Faculty of Pharmacy, Medical University, Sofia 1000, Bulgaria*<sup>2</sup>*Department of Physical Chemistry, University of Sofia, Sofia 1126, Bulgaria*

Pilocarpine - the drug most frequently used for the treatment of the dangerous eye disease glaucoma characterized by an increased intraocular pressure, has been applied in pharmacology as 1 to 5% aqueous solutions in the form of the salt pilocarpine hydrochloride. Pilocarpine solutions are most stable at pH = 4.0 to 5.0. Because of their acidity, however, they cause additional tear formation and enhanced washing away from the eye, which leads to a decreased therapeutical effect.

In the present work the possibility to include cellulose acethophtalate (CAP) as a prolonged acting pilocarpine carrier in ophthalmic formulations was investigated. The viscosity of CAP-containing dispersions increases with the increase in pH from 4.5 (at which CAP is insoluble in water) to 7.2 (pH of the tear film, at which CAP is water soluble). Thus, when coming into contact with tears such dispersions cannot be easily washed away and remain in the eye for a longer period of time. Their particles form a micro reservoir of the drug in situ of high viscosity. This mechanism prolongs the action of the included drug and the respective pharmacological effect.

The influence of different surfactants on the possibility to obtain fine dispersions with a comparatively high percentage of cellulose acethophtalate (CAP) was studied. A method for obtaining concentrated dispersions of CAP including the drug pilocarpine hydrochloride was proposed.

Thin liquid films formed from aqueous CAP dispersions on a glass surface were used as a model of tear films in the eye. The film thickness was determined by the microinterferometric method. The average value of the critical thickness of rupture was found in cases when rupture existed. The kinetics of thinning was studied and discussed. On that basis certain dispersions were chosen as appropriate for further investigations as possible prolonged acting pilocarpine carriers in ophthalmic formulations.

A method was developed for the approximate estimation of the average size of CAP particles in the film on the basis of photomicrograms. The average particle radius was 172 nm, which is small enough not to cause physical irritation to the eye.

**878.H5****BIOCOMPATIBLE AMPHIPHILIC DIBLOCK COPOLYMERS AS STABILIZING AGENTS FOR THE PREPARATION OF MICRO- AND NANOSPHERES FOR PARENTERAL ADMINISTRATION****Ruxandra Gref<sup>1</sup>, Phillippe Bouillot<sup>1</sup>, Edith Dellacherie<sup>1</sup>, Valery Babak<sup>2</sup>, Irina Lukina<sup>2</sup>**<sup>1</sup>*ENSIC INPL, 1, Rite Grandville, B.P. 451, 54001 Nancy Cedex, France*<sup>2</sup>*INEOS RAS, 28 Vavilova str., Moscow 117813, Russia*

Biodegradable nanospheres and microspheres for the controlled release of drugs were obtained from oil-in-water (o/w) emulsions by evaporation of organic solvents (methylene chloride, ethylacetate, etc.).

To exclude the surfactants (not always biocompatible) from the preparation of the o/w emulsions, we synthesized a family of amphiphilic biocompatible diblock copolymers: polyethylene glycol-poly(lactic acid)(PEG-PLA), which were further used as emulsifying and stabilizing agents. PLA is hydrophobic and biodegradable, whereas PEG is hydrophilic and bioeliminable. By varying the PEG molecular weight from 2 to 20 kDa, the PLA molecular weight from 0.56 to 10 kDa, and the polarity of the organic phase, we could control the interfacial tension at the oil-water interface and reduce the droplet size of the o/w emulsions.

The critical concentration of aggregation of the diblock PEG-PLA copolymers in water was determined by surface tension measurements and DSC. The stability of the emulsion to rupture was assessed by the measurement of the stability (the life-time before rupture) of microscopic liquid films formed by the method of contact interactions between two droplets of the organic phase with the diameters of ~ 1 mm in the aqueous phase under the strict control of the physico-chemical parameters: concentration of polymer, time of formation of polymer adsorption layers, pH, electrolyte concentration, etc.

The stabilization of the emulsion droplets against coagulation and coalescence in the course of emulsification and solvent evaporation procedures was realized by the steric repulsion between hydrophilic

PEG tails of the copolymer macromolecules forming a protective adsorption and finally coating layer of microparticles. The range of HLB of diblock PEG-PLA (depending on the relative length of the two blocks) and the polarity of the organic phase was determined to prevent the coagulation and partial coalescence of droplets and to obtain perfectly spheric particles of well defined size. The optimum length of PEG tails was estimated on the base of the modern theories of steric stabilization.

Due to the hydrophilic coating thus obtained, which reduces protein adsorption and interaction with phagocytic cells, these particles may find many potential therapeutic applications.

## 879.H5

### MOLECULAR INTERACTIONS AND VESICLE TARGETING TO BIOFILMS

Malcolm N. Jones, Michael Kaszuba, Anne M. Robinson and Neil M. Sanderson  
*School of Biological Sciences, University of Manchester, Manchester M13 9PT, UK*

With the ultimate goal of targeted drug delivery, phospholipid vesicles (unilamellar liposomes of approximately 100 nm diameter) have been prepared from phosphatidylcholine (DPPC) in combination with a range of charged lipids including phosphatidylinositol (PI), stearylamine (SA), and dioctadecyldimethylammonium bromide (DDAB) and their adsorption to a range of biofilms of oral and skin-associated bacteria immobilised on a solid surface has been investigated. Both anionic lipids (PI) and cationic lipids (SA and DDAB) when incorporated into DPPC vesicles facilitate adsorption. In the case of PI-containing vesicles optimum levels of PI are found for maximum adsorption to numerous bacterial biofilms. This effect can be explained in terms of a balance of interactions between the PI head groups and the surface macromolecules in the bacterial glycocalyx. Ionic interactions between charged vesicle and bacteria are essentially nonspecific and are mediated by ionic strength, however specificity can be introduced by chemically linking antibodies raised to cell surface antigens to the vesicle surface to produce immunoliposomes. Immunoliposomes have been prepared to the oral bacteria *Streptococcus oralis*. The targeting of the immunoliposomes has been studied as a function of vesicle concentration, vesicle charge and surface density of the antibody. The immunoliposomes have been used to deliver the bactericides Triclosan and chlorhexidine to inhibit the growth of the bacteria from biofilms and the relationship between targeting and bacterial growth inhibition investigated. It has been shown that vesicles are a superior means of drug delivery relative to the use of 'free' drug when the drug concentration is low and the times of exposure of biofilm to the vesicles or free drug is short (~minutes).

## 880.H5

### LOW AMOUNTS OF PEG-LIPID INDUCE CUBIC PHASE IN PHOSPHATIDYLETHANOLAMINE DISPERSIONS

Rumiana Koynova<sup>1</sup>, Boris Tenchov<sup>1</sup> and Gert Rapp<sup>2</sup>

<sup>1</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

<sup>2</sup>*EMBL - Outstation Hamburg, D-22603 Hamburg, Germany*

Using liposome preparations for *in vivo* drug delivery is a long-standing goal of numerous scientific researches. Some of the problems to be solved upon developing such preparations include increasing their time in blood circulation and controlled-release formulations. Important recent advances in liposome design in these respects represent the incorporation into liposomes of phospholipids with poly(ethyleneglycol) (PEG) chains covalently attached to their polar head group (PEG - lipids) for prolongation of the circulation time, and the utilizing of cubic mesomorphic liquid crystalline phases formed in lipid / water systems for controlled drug release.

Here we report an intersection of these two approaches in liposome design which may prove useful for the further investigations in the field of controlled drug delivery. By using time-resolved X-ray diffraction we demonstrate that low amounts (5-10 mol%) of a phospholipid with two saturated hydrocarbon acyl chains 14 carbon atoms long and PEG550 chain covalently attached to its phosphoethanolamine polar head group, DMPE(PEG550), induce spontaneous formation of a cubic phase with lattice constant 20.5 nm (cubic aspect #8, space group Im3m) in aqueous dispersions of dielaidoylphosphatidylethanolamine (DEPE). This phase displays a highly resolved X-ray diffraction pattern with 17 low-angle reflections. The cubic



phase was found to intrude in the temperature range between the lamellar liquid crystalline ( $L_\alpha$ ) phase and the inverted hexagonal phase ( $H_{II}$ ) known to form in pure DEPE/water dispersions. A higher DMPE(PEG550) amount of 20 mol% eliminates the non-lamellar phases in the temperature scale up to 100°C. DMPE grafted with PEG5000 only shifts the  $L_\alpha$ - $H_{II}$  transition of DEPE to higher temperatures but does not promote formation of cubic phase. These findings indicate that, consistent with their bulky head groups, the PEG-lipids decrease the tendency for negative interfacial mean curvature of the DEPE bilayers.

## 881.H5 PLA-PEG NANOPARTICLE DISPERSIONS FOR DRUG DELIVERY

T. Riley, C.D. Xiong, A.E. Hawley, S. Stolnik, M.C. Garnett, Th.F. Tadros, L. Illum and S.S. Davis  
*Department of Pharmaceutical Sciences, University of Nottingham, Nottingham, England*

Biodegradable long circulating colloidal carriers have attracted recent interest in the field of drug delivery, as vehicles for targeting a drug to its pharmacological site of action. Long circulating properties are achieved by the presence of an adsorbed or grafted steric barrier (for example, polyethyleneglycol). This steric layer acts to prevent the adsorption of circulating blood components which ordinarily facilitate the recognition and subsequent engulfment of colloidal carriers by the macrophages of the reticuloendothelial system (RES).

Recently, polylactide-polyethylene glycol (PLA-PEG) AB copolymers have been used to produce biodegradable sterically stabilised nanoparticles. In an aqueous medium, the PLA blocks aggregate to form the core of the particle and the PEG chains extend into the surrounding media to give the steric barrier. In the present work a series of PLA-PEG copolymers with a fixed PEG chain length ( $M_w$  5 kDa) and a PLA segment of varying length ( $M_w$  3 - 110 kDa) have been synthesised by a ring opening polymerisation of d,l-lactide using stannous octoate as a catalyst.

These copolymers were used to produce aqueous dispersions of spherical particles by a simple phase separation technique. A wide range of particle sizes (30-150 nm) has been achieved by varying the molecular weight of the PLA block. The series exhibits a marked trend of reduced stability towards the addition of electrolyte as the hydrodynamic radius of the particle is increased. In contrast, *in vivo* studies have shown that following intravenous injection the larger particles remain in the systemic circulation for a prolonged period of time, whereas the smaller particles are rapidly cleared and accumulate in the liver and spleen. The blood circulation times of the largest PLA-PEG nanoparticles are comparable to those previously obtained for similarly sized polystyrene particles surface covered with PEG chains.

The particle size, corona layer thickness and PEG surface density, all of which are interdependent, are likely to play an important role in determining the biological fate of these particulate systems. Hence studies are now being focused on a comprehensive evaluation of the colloidal properties of the PLA-PEG nanoparticle dispersions. The association number of copolymer molecules per particle has been determined by obtaining the molecular weight of the particle from static light scattering measurements. Viscoelastic measurements of concentrated PLA-PEG dispersions have been used to provide an estimate of the PEG layer thickness (approximately 10 nm) from the critical volume fraction where the polymer chains just begin to overlap. In addition for the small PLA-PEG particles, the low slope of a log-log plot of the storage modulus ( $G'$ ) as a function of particle volume fraction suggests that the PEG chains are highly compressible.

It is hoped that a thorough physicochemical characterisation of these PLA-PEG systems will lead to an improved understanding of the role of PEG in achieving long circulating colloidal carriers for drug delivery.

## 882.H5 POLYMERIZED LIPOSOMES AS POTENTIAL DRUG DELIVERY SYSTEMS

E.I. Vargha-Butler and G.K. Xiang  
*College of Pharmacy, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 3J5*

Traditional multilamellar (MLV) liposomes have several characteristics which might render them as desirable vesicles to deliver both hydrophobic and hydrophilic drugs. However, most liposomes are not stable and unwanted leakage of the encapsulated drug often occurs due to structural changes of the

multilayers during storage. Polymerization of liposomes prepared from unsaturated lipids was therefore considered, because in these liposomes the bilayer-forming phospholipid molecules are linked together by covalent bonds, which should provide an improved stability to the membrane.

MLV liposomes and polymerizable liposomes were prepared by means of the hydration method, using saturated soyphosphatidylcholine (SPC) and unsaturated diacetylenic lipid, respectively. The unsaturated lipid was 1,2-bis (10,12-tricosadiynoyl)-sn-glycero-3-phosphatidylcholine ( $\text{DC}_{8,9}\text{PC}$ ) with a hydrocarbon chain of  $\text{C}_{23}$ . All liposome samples (saturated and unsaturated) contained 10 mg/ml lipid. Both empty and drug loaded vesicles (with varied drug input concentration) were studied. Naproxen, a non-steroidal, antiinflammatory drug, as model drug ( $\text{C}_{14}\text{H}_{14}\text{O}_3$ , MW= 230.26) was encapsulated in both types of vesicles. Liposomes prepared from the diacetylenic lipid were then polymerized in a photoreactor by irradiating the samples with UV light at a wavelength of 254 nm for 4 hours. The progress of the polymerization was followed by taking samples at selected time intervals and analysing the concentration of the free lipid remained non-polymerized, by means of HPLC method. The extent of drug encapsulation and release was also measured in the different samples and the results obtained for the traditional and polymerized liposomes were compared.

The first major difference between traditional and polymerizable liposomes was observed *before* the polymerization. Examination under light microscope showed that while the traditional multilamellar vesicles had the usual spherical "donut" shape (with approx. 0.5 to 10-15  $\mu\text{m}$ , in diameter), liposomes prepared from the diacetylenic lipids first formed metastable, distorted spheres, which, while cooling through the lipid's phase transition temperature (43°C), turned into long needles. Electronmicroscopic studies revealed that the 'needles' were 'microcylinders', open-ended tubules, which had a length of 8 to 13  $\mu\text{m}$  and their diameter varied between 0.6 to 0.8  $\mu\text{m}$ . The tubules had a thin wall composed of one to several bilayers, which might overlap each other. *During* the polymerization it was observed, that the dispersion of the originally white tubules turned into pink  $\rightarrow$  red  $\rightarrow$  dark red, indicating that oligomers, then polymers were formed which had chromophores in the visible spectrum. The electronmicroscopic analysis showed, that the structure of tubules also changed *during/after* polymerization, i.e. they became disordered, some of them unfolded or even broken down. The maximum degree of polymerization achieved with these liposomes was around 40 percentage of the (input) lipid. Results obtained with drug loaded polymerized liposomes indicated, that with increasing input concentration of Naproxen, the encapsulation and release were increasing, while the extent of the polymerization was decreasing. Comparison between the traditional MLV and the tubular, polymerized liposomes showed that the traditional liposomes were better as drug delivery vesicles, but it seems that the disadvantage of the polymerized ones is due to some structural properties, such as the open-ends of the tubules and their elongated shape. When the tubule formation could be prevented by selecting different unsaturated lipid, other preparation method and/or reducing the liposome size, the polymerized liposomes will have their potential to deliver drug.

### **883.K1 BANK OF OPTICAL DATA FOR DISPERSE SYSTEMS AS INFORMATIVE BASE FOR COLLOID SCIENCE, MEDICINE, PHARMACY AND ENVIRONMENTAL SENSING**

**Alexandra G. Bezrukova**

*Dept. of Biophysics, Phys.-Mech. Faculty, St. Petersburg State Technol. Univ., St. Petersburg 195251, Russia*

Large-scale molecular assemblies such as protein aggregates, nucleoproteins, liposomes carried some substances lipoproteids, liquid crystals with surfactants, metallic, clay and cell dispersions or different engineered nanostructures could be considered as disperse systems (DS). Multiparametric nondestructive optical analysis can provide further progress in studies of these complex objects. It includes the simultaneous analysis of DS by different optical methods such as refractometry, absorbance, fluorescence, light scattering (integral and differential, static and dynamic, unpolarized and polarized). The methodologies for the simultaneous analysis of multiple spectroscopic experimental data are developed as "global" and "target" analysis. In the case of optical data for DS the "global" analysis can help to investigate the fundamental processes of aggregation, flocculation, coalescence, heteroaggregation, fractal aggregation, etc. The "target" analysis can help to create sensing elements as on the base of DS, so for DS on-line control. It is in accordance with fiber optics development. For such purposes creation of Bank of Optical Data for Disperse Systems (BODDS) is one of the steps. BODDS includes three sections: 1) experimental optical data; 2) theoretical optical data; 3) the data of different physico-chemical methods for disperse systems. The main idea of BODDS collection is the operation with data inside it and the solving of inverse physical problem by different ways. The majority of natural and technological DS are multicomponent (MTC) and multimodal (MTM). While there exist enough knowledge about the behaviour of monocomponent (MNC) DS the study of MTC MTM DS is the task of future. The BODDS aim is to accumulate data from different MNC DS and to elaborate some methods for MTC MTM DS further study. Natural water and air also could be considered as MTC MTM DS. During the analysis of unknown multicomponent disperse system, for example, water with impurities of metals, oil, dangerous viruses or bacteria, the comparison of measured parameters with known one can help us to identify the unknown system.

### **884.K1 IMPROVED OPHTHALMIC SOLUTION OF INDOMETHACIN ON THE BASIS OF PLURONICS<sup>R</sup>**

**E. Dimitrova, Sv. Bogdanova, M. Kassarova, M. Mitcheva, E. Minkov**

*Faculty of Pharmacy, University of Medicine, 1000 Sofia, Bulgaria*

The influence of Pluronic 68<sup>R</sup> and Pluronic 127<sup>R</sup> on the indomethacin aqueous solubility, stability and irritation on rabbit eyes were investigated to improve the properties of the recently reported 0.5% indomethacin aqueous ophthalmic solution (I) (Int. J. Pharm., 1993). (I) was formulated on the basis of hydrotropic and micellar interactions of the drug with tween 80 and propylenglycol. The Pluronic<sup>R</sup> were used in a concentration range (from 3% up to 15%) to evaluate the optimal concentration of the surfactant assuring the highest indomethacin solubility, optimal viscosity and physical stability of the aqueous solution before and after sterilization. The stability studies carried out at "stress" conditions and constructed Arrhenius plots predicted a shelf life over 1 year. In conclusion Pluronics<sup>R</sup> can be successively used as a non-irritating vehicle of 0.5% indomethacin aqueous solution for ophthalmic use.

### **885.K1 SILICA-SURFACTANT COMPOSITE THIN FILMS AS SUBSTRATES FOR CONTROLLED RELEASE OF ACTIVE INGREDIENTS**

**M. Ferrer, V. Bekiari and P. Lianos**

*University of Patras, Engineering Science Dept., 26500 Patras, Greece*

Silica-surfactant composite films have been made by the sol-gel method by adding partially hydrolysed tetramethoxysilane or tetraethoxysilane to aqueous micellar solutions (ref. M. Ogawa, *J. Am. Chem. Soc.* 1994, 116, 7941; M. Ferrer and P. Lianos, *Langmuir*, in press). Micellar solutions were made by

trying three surfactants: a cationic, cetyltrimethylammonium bromide (CTAB); an anionic, sodium dodecyl sulfate (SDS); and a non-ionic (Triton X-100). Thin transparent films were obtained by dip-coating at an early stage of gelation. The films have been characterized by various methods with particular emphasis on fluorescence probing. Models compatible with the results for the structure of the films will be presented. These materials allow slow release of embedded organic molecular species. The process has been monitored by absorption spectrophotometry. Relevance to drug delivery will be stressed.

## 886.K1 COLLOID TECHNOLOGIES IN THE CHEMISTRY OF SURFACTANTS

Polkovnichenko I.T., Germasheva I.I.  
NPAO "SintezPAV", Russia

Colloid-chemical characteristics of surfactants can be effective technological parameters in the processes of synthesis of surfactants, isolation of the goal product, separation of mixtures. One of such parameters can be the Krafft temperature. Based on the differences of the Krafft temperatures of sodium dodecyl sulphate and surface-active impurities, a new technology has been developed for isolation of sodium dodecyl sulphate with predetermined purity characteristics from the sulphation reaction mixture of individual dodecanol - the temperature region of the existence of the pure dodecyl sulphate is determined by the conductivity polytherm, and it serves as a technological parameter. A variation of the technology can be the isolation of dodecyl sulphate from the sulphation reaction mixture of  $C_{10}$ - $C_{14}$ ,  $C_{12}$ - $C_{16}$  and other alcohol fractions. Depending on the solvent, a technology of the isolation of a crystalline DDSNa can be accomplished, with the accumulation of impurities in the solution or, on the contrary, the impurities can be separated with concentrating DDSNa in the solution. One of the methods to obtain new salt forms of alkyl-sulphates, i.e. lithium, potassium, magnesium, copper, barium salts etc, is the exchange reaction of the basic DDSNa with the corresponding anorganic salts. The method developed allows to determine the isolation temperature of the pure goal product and to render the process strictly controllable. Similarly, mono- and disodium salts of monoalkylphosphates can be separated in the reaction mixture of alkyl phosphates. The possibility of carrying out the process continuously is an important advantage.

## 887.K1 WATER SOLUBILITY ENHANCEMENT FOR PHARMACEUTICALS THROUGH THE SURFACTANT MOLECULAR COMPLEX FORMATION

Nahoko Iimura, Hiroyuki Wakabayashi and Hirotaka Hirata  
Niigata College of Pharmacy, 2-13-5 Kamishin'eicho Niigata, 950-21, Japan

In these few years we have succeeded in the stable isolation of many kinds of crystalline molecular complexes between surfactants and various additives. To date we have also obtained abundant structural

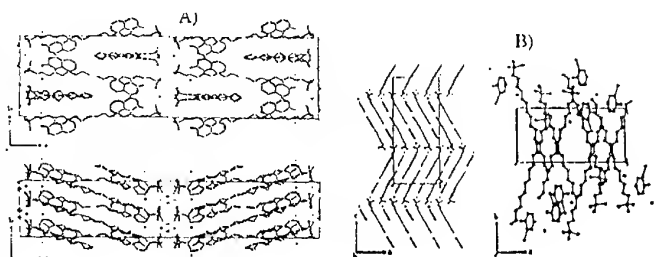


Figure 1. Crystal packings of the anionic and the cationic surfactant molecular complexes on each projection, A) sodium octyl sulfate/2-naphthol and B) CTAB/o-iodophenol, respectively.

knowledge of the surfactant complexes by X-ray analysis. Some typical structures are presented in Figure 1. The crystalline surfactant molecular complexes which are mainly yielded from aqueously treated conventional solubilized solution systems at cool conditions are, on warming, instantaneously dissolved and realize the original solubilization systems again, of course, restoring all the solution characteristics. It directly implies that the phenomenon so far referred to as "solubilization" is not special but just a common one like daily observable dissolution of any crystalline salt. On the basis of these findings, we have developed a very

effective technique that through the surfactant complex formation, all of those additive species which are almost insoluble or sparingly soluble to water are modified to species of much higher water solubility. We applied the procedure to several pharmaceuticals which are difficult to dissolve in water and obtained fruitful results of making them easily soluble as shown in Table 1, with expectation of wide improvement to pharmaceuticals in the amount and the form of dosage, routes of administration, pharmacokinetics and -dynamics, etc.

Table 1. Water solubly modified pharmaceuticals in the systems of the molecular complex formation with various surfactants:

Surfactant	Pharmaceutical	Complex molar ratio (Surf./Pharm)	Preparation medium
Polyoxyethylenecetyether	Phenobarbital	1/3	CHCl <sub>3</sub> /H <sub>2</sub> O
Ammonium dodecyl sulfate	Famotidine	1/1	MeOH/H <sub>2</sub> O
"	Sulpiride	2/3	"
Potassium dodecyl sulfate	Ethenzamide	1/1	H <sub>2</sub> O
"	Flopropione	1/1	"
Cetyltrimethylammonium bromide (CTAB)			
"	Isopropyl- antipyrine	2/1	"
Cetyltrimethylammonium sulfosalicylate	Naproxen	3/2	"
"	Dipyridamole	3/1	"
Cetylpyridinium thiocyanate	Naproxen	2/1	"

### 888.K1 STUDY ON POLYOXYETHYLENE ALKYL ETHER SERIES NON-IONIC SURFACTANTS AS POTENTIAL DRUGSOLUBILIZERS

M. Kassanova<sup>1</sup>, St. Shenkov<sup>2</sup>, J. Baranovsky<sup>2</sup>, E. Minkov<sup>1</sup>, M. Mitcheva<sup>1</sup>

<sup>1</sup>Faculty of Pharmacy, University of Medicine, 1000 Sofia, Bulgaria,

<sup>2</sup>Bulgarian Academy of Sciences, Central Laboratory of Polymers

Several series of polyoxyethylene alkyl ethers were studied to evaluate their solubilizing capacity as well as the factors influencing their micellar properties. There have been investigated ethoxylated alcohols (capril, lauryl, octyl, palmityl, cetyl, stearyl) with different length of the oxyethylene chain (2-80 units ethylene oxide). The cloud-point, as well as the critical micelle concentration were determined by surface measurements to optimize the ratio between the hydrophobic chain length and the number of the ethylene oxide units. The phase diagrams of threephase systems with vitamin A, vitamin E, liquid paraffine, sunflower oil and peppermint oil were constructed to determine the zone of the solubilization. The micellar structure of the optimal molecule (polyoxyethylene (13)cetyl ether) was studied in detail by means of viscosimetric-, density- and light scattering measurements. It was established that all aqueous solubilizes were thermodynamically stable. The good solubilizing activity and the established low toxicity in mice make this compound a potential solubilizer of drugs.

### 889.K1 SURFACE ACTIVE PROPERTIES IN LIGHT DUTY LIQUID DETERGENTS

Farrokh B. Malihi

Research & Development Department, Malihi & Associates

A study of surface active properties in light duty liquid detergents containing anionic, nonionic and amphoteric surfactants is reported. Dependence of the efficiency and effectiveness of surface tension

reduction on surfactant structure, temperature and water/hardness is discussed. The effect of certain electrolytes used in detergent systems including; phosphate, silicate, and sulfate is studied. These results indicate a significant reduction in surface tension profile in the presence of these electrolytes with the sodium tripolyphosphate having the most pronounced effect.

Synergistic effects are explored in mixed surfactant systems containing anionic-anionic, anionic-nonionic and anionic-amphoteric surfactants. These results are compared with application properties i.e. foam volume and foam stability in the presence of oily soils. Synergistic effects were observed particularly in the case of anionic-amphoteric system where a significant reduction in surface tension profile was shown at 4:1 anionic/amphoteric mixture ratio. Such effects may explain certain beneficial application properties in household and personal care product formulations.

## **890.K1 PEPTIDE MAPS OF WHITE EGG PROTEIN PROTEOLYSIS IN THE COEXISTENCE SOLUTION OF PROTEASE AND SURFACTANTS**

**Michiko Shigeta, Harumi Yoshikawa and Junji Takahashi**

*School of Home Economics, Osaka University of Education, 4-88 Minamikawahori,  
Tennoji-ku, Osaka Japan, 543*

Proteolytic enzyme as detergent additive is not clear in its effect. Coexistence solution of protease and surfactant still have much conjecture if inhibition arise or not. In this work, we examined the proteolysis of alkaline protease (*Bacillus subtilis* BPN) containing surfactant (SDS, LAS, AOS, AES, AE). Native white egg was used as substrate. White egg protein is composed of ovalbumin (MW. 45,000), lysozyme, which is highly stabilized by 4 disulfide bridges, is capable of withstanding (MW. 14,500) and so on. Protein and peptide fragments produced by proteolysis were separated using SDS-polyacrylamide gel electrophoresis (SDS-PAGE) by 10~20% gradient gel slab with discontinuous system. These gels can cover the molecular weight range from 3,000 to 100,000 very well. The major findings of this work may be summarized as follows:

Ovalbumin proteolysis of this protease was more accelerated with anionic surfactants than without them. In particular, coexistence solution of protease and AOS produced small fragments of peptide (less than MW. 10,000). Lysozyme was not hydrolyzed by only protease but the addition of anionic surfactants proteolyzed them. Coexistence solution of protease and nonionic surfactant AE could not accelerate the proteolysis of white egg protein. These results suggest that adsorption of anionic surfactants to white egg protein cause some change of conformation, then protease can easily hydrolyze the white egg protein.

## **891.K1 MAGNETIC NANOPARTICLE RELAXATION MEASUREMENT AS A NOVEL TOOL FOR THE BINDING SPECIFIC EVALUATION OF IMMUNOASSAYS**

**W. Weitschies<sup>1</sup>, R. Köttitz<sup>2</sup>, T. Bunte<sup>3</sup>, T. Rheinländer<sup>1</sup>, L. Trahms<sup>2</sup>**

<sup>1</sup>*Institut für Diagnostikforschung GmbH, Spandauer Damm 130, D-14050 Berlin, Germany*

<sup>2</sup>*Physikalisch-Technische Bundesanstalt, Abbestraße 2 - 12, D-10587 Berlin, Germany*

<sup>3</sup>*Research Laboratories of Schering AG, Müllerstraße 170, D-13345 Berlin, Germany*

The analysis of biological binding reactions is usually achieved by labeling one of the reaction components with radioisotopes, enzymes or fluorescence dyes. In particular the quantitative analysis of substances by the immunoassay technology, where the specificity of the reaction between antibodies and their antigens is used, is of outstanding importance in medicine and biology. Hence, using radioisotopes, enzymes or fluorescence dyes, the signal generated by the label is mostly not influenced by the binding reaction. Therefore, separation procedures between bound and unbound reaction components are mostly inevitable in order to quantify the amount of bound substance.

Here, we present the use of magnetic nanoparticles as labels to antibodies in the detection of reactions between antibodies and their antigens. After the removal of a magnetizing field these labels show a time dependent magnetization (relaxation). The presented experiments demonstrate that the measurement of

magnetic nanoparticle relaxation signals provide a novel tool for the quantitative determination of immunoassays. The binding specificity of this detection method is achieved by the influence of the biological binding reaction on the dominating relaxation process of the magnetic nanoparticles.

Unbound magnetic nanoparticles relax according to rotational diffusion (Brownian relaxation) with a time constant in the range of 50  $\mu$ s. For magnetic nanoparticles that are bound by the binding reaction between the coupled antibody and its solid phase bound antigen this process is hindered and the Néel relaxation of particles with relaxation times longer than 50  $\mu$ s becomes detectable. In order to achieve high sensitivity the measurements were performed using Superconducting Quantum Interference Devices (SQUIDS) as magnetic field sensors.

## 892.K2 EFFECTS OF PICKLING, TIME AND ELECTRODIALYSIS DESALINATION ON FUNCTIONAL PROPERTIES OF SALTED DUCK EGG WHITE

Jan-Jeng Huang<sup>1\*</sup>, Jenn-Shou Tsai<sup>2</sup>

<sup>1</sup>Dept. of Food Industry, National Chiayi Institute of Agriculture, Chiayi, Taiwan, R.O.C.

<sup>2</sup>Dept. of Marine Food Science, National Taiwan Ocean University Keelung, Taiwan, R.O.C.

Salted duck egg was prepared by coating fresh duck egg with laterite and sodium chloride. The effects of different lengths of pickling time and electrodialysis desalination on foaming, emulsifying and gelling properties of salted duck egg white (SDEW) were investigated. The pH was decreased from 9.3 to 7.1, Zeta potential was decreased from - 48.3 to -26.4 (mV), NaCl content increased from 0.49% to 7.32% and surface hydrophobicity increased from 177 to 372 (Se/100mg protein) after pickling for 8 weeks. After electrodialysis desalination treatment the pH of SDEW was slightly increased and Zeta potential was not significantly changed; however the NaCl content was reduced by 95% and surface hydrophobicity decreased by 30%. The SDS-PAGE pattern showed the same distribution of protein molecules. Electrodialysis desalination treatment did not affect emulsifying ability. The foaming ability and stability of SDEW decreased with increasing pickling time, but increased with electrodialysis desalination treatment. The gel strength of SDEW increased with pickling time, but decreased after electrodialysis desalination treatment.

## 893.K2 THE STRUCTURAL PROPERTIES OF $\beta$ -CASEIN AND THEIR INFLUENCE ON INTERFACIAL AND FUNCTIONAL PROPERTIES

Fiona A. Husband, Alan R. Mackie, Peter J. Wilde

*Institute of Food Research, Norwich Research Park, Colney, Norwich, NR4 7UA. UK.*

Most proteins used for the formation and stabilisation of food dispersions are globular in nature, containing a significant degree of secondary structure. This usually results in the formation of a viscoelastic network at the interface, stabilising emulsion droplets and foam gas bubbles from coalescence.  $\beta$ -casein however, possesses very little secondary structure, which allows rapid adsorption and rearrangement at the interface, resulting in good foam and emulsion formation ability. However, the lack of secondary structure means that the strength of the viscoelastic network at the interface is much lower than that of its globular counterparts, and it also has unusual dynamic properties. Consequently, the stability of foams formed with  $\beta$ -casein tends to be rather low. Emulsion orthokinetic stability measurements however show that emulsions stabilised by  $\beta$ -casein have much greater stability than many globular proteins.

Despite the lack of structure,  $\beta$ -casein does have specific domains with distinct hydrophobic and charge properties, therefore we have attempted to correlate the unusual interfacial behaviour and functionality of  $\beta$ -casein, with its conformational properties. Using a variety of interfacial techniques including interfacial tension, surface rheology and film thickness determination on native and modified  $\beta$ -casein, we found that certain regions of the protein, particularly the phosphorylated loop, played a vital role in the functional properties.

## 894.K2 EFFECT OF THE pH AND ANION TYPE ON THE SURFACE PROPERTIES OF WHEAT GLIADINS AND MIXED WHEAT GLIADINS - PEA GLOBULINS DILUTED DISPERSIONS

Zenon Kedzior, Anna Pruska-Kedzior, Ewa Drzewiecka

*University of Agriculture, Institute of Food Technology, Poznan, Poland*

The effect of natural organic anions (formic, acetic, lactic and propionic acids) and the pH (3.0, 3.5 and 4.0) on tensioactive properties of wheat gliadin dispersions was studied. The effect of protein - protein and protein - protein - polysaccharide interactions was also examined for mixed systems: wheat gliadin - pea globulin dispersions and wheat gliadin - pea globulin - polysaccharide (guar gum and/or xanthan gum) dispersions. Two Polish wheat varieties were used to prepare gliadin fraction: Begra (strong gluten system) and Wilga (weak gluten system). Gliadins were extracted following Coates and Simmonds method: using 0.01 M pyrophosphate buffer pH 7.0 to remove albumins and globulins and 0.05 M acetic acid to extract the gliadin fraction. Pea globulins were obtained by extraction of pea flour with orthophosphate buffer pH 7.0 and exhaustive dialysis of the pea protein extract against distilled water. Gliadin dispersions of concentration 0.01, 0.025, 0.05, 0.075 and/or 0.1% respectively were prepared using formic, acetic, lactic and propionic acids solutions of molarities assuring final dispersions of pH 3.0, 3.5 and/or 4.0 respectively. Additions of 0.3, and/or 3.0% of pea globulins and 0.5% of guar or xanthan gums (as referred to the dispersion dry weight) were applied. Surface tensions of the dispersions were measured. Wilhelmy plate and du Nouy ring methods of measurement were compared. Surface tensions of the dispersions varied in the range from 40 to 50 mN/m. Effects of the surface tension changes related to the gliadin type (wheat variety), the pH, type of anion used as well as these caused by the interactions of gliadins with pea globulins and the polysaccharides used were observed.

## 895.K2 EFFECT OF PECTIN ON THE ELECTROKINETIC PROPERTIES AND CLOUD STABILITY OF PULP SUSPENSIONS FROM APPLES

Plamen Mollov<sup>1</sup>, Ivana Petkanchin<sup>2</sup>, Emil Maltchev<sup>1</sup>

<sup>1</sup>*Higher Institute of Food and Flavour Industries, Plovdiv, Bulgaria*

<sup>2</sup>*Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The effect of native pectin and apple pectin preparations with three different degrees of esterification (H = 73 %, M = 54 % and L = 45 %) upon the electrokinetic properties and cloud stability of pulp suspensions from apples has been studied.

The electrokinetic potential ( $\zeta_R$ ) of suspended particles increased in the presence of pectin depending on its:

- concentration (C) by the following equation:  $\zeta_R = a_0 + a_1 \cdot \ln C + a_2 \cdot (\ln C)^2$ ;
- degree of esterification in the order:  $L \geq M > H$ .

It has been shown that the native pectin exerts an essential influence on the adsorption ability of the pectin added and the electrokinetic potential of tissue particles.

The adsorbed pectin increased the sedimentation resistance of suspended particles and the cloud stability of studied suspensions but the effect of the native pectin was more significant.

## 896.K2 INFLUENCE OF FREE CALCIUM AND OF CALCIUM COMPLEXES ON THE COLLOIDAL STABILITY OF SOYBEAN MILK

P. Van der Meeren and J. Vanderdeelen

*University of Ghent, Faculty Agricultural and Applied Biological Sciences, Dept. of Applied Analytical and Physical Chemistry, Laboratory of Applied Physical Chemistry, Coupure Links 653, B-9000 Gent, Belgium*

During recent years, the consumption of soybean milk has steadily increased. The major advantages of this milk of vegetable origin as compared to cow's milk are the absence of both cholesterol and lactose. A major disadvantage, however, is the very low calcium content.



In order to overcome this shortcoming, the addition of soluble calcium salts may seem a logical solution. However, severe flocculation and curd formation was observed at calcium concentrations exceeding 5 mM. Electrophoretic mobility measurements revealed that this behaviour was primarily due to the pronounced reduction of the Coulomb repulsion between negatively charged soybean milk droplets. It follows that the concentration of free calcium ions should be limited, which may be accomplished by complexation. Citrate was preferred because the equilibrium constants of the calcium-citrate complex are quite high and because it is food-compatible. Photon correlation particle sizing experiments as a function of storage time indicated that stable soybean milk dispersions could be prepared containing 30 mM of calcium ions, provided that at least an equimolar concentration of sodium citrate was added. The results obtained could be explained by DLVO theory, keeping account of the free ion concentrations. The latter were calculated from the overall concentrations, from the dissociation constants of citric acid and from the equilibrium constants for calcium complexation by citrate, keeping account of the electroneutrality constraint.

### 897.K3 BIOSURFACTANT PRODUCTION AND ENHANCED OIL RECOVERY

H. Bastardo

*Universidad Central de Venezuela I.Z.T., P.O.B. 47058, Caracas 1041-A, Venezuela*

Enhanced Oil Recovery (EOR) is actually considered as the tertiary phase of production in wells and recuperation of crude oil in pits. Experimental studies for oil recovery processes reveals that more than one mechanism is often used, and it is known that the surfactant polymer production is the more important, because of this organic substances are capable to reduce the interfacial tension and increasing of water viscosity. Assays were done to produce tensioactive organic compounds from bacterial metabolic activities. Used a selected pool of bacteria which were capable of crude oil degradation and also emulsifying the remaining crude oil fractions. Was used a carbon source of low molecular weight as energetic substrate. The kinetic of growth of bacterial pool, the surfactant production and the ability of reduce the surface tension of the water (tensioactivity). The assays were made in order to scale the tensioactive compounds production from 1 L to 1000 litres. The changes occurred in the different fractions of crude oil, surfactant characteristics and emulsification of crude oil capacity, was analyzed. The bacterial pool selected was capable to growth at 50 °C; 5 - 7 pH units range and undergoes salinity of 50 - 70 parts per million of NaCl. The surfactant production seems to be different when alternative energy sources and the physico-chemical conditions are changed. Also the emulsion rate of crude oil in the different assays is different, probably related with the production of different kinds of surfactant by bacterial pool.

### 898.K3 THE STUDY AND APPLICATION OF THREE-PHASE FOAMS IN OIL AND GAS PRODUCTION PROCESSES

Dolgov X.V, T.L. Dong, Carimov M.Ph., T.S. Phiet

*Research and Design Institute for offshore Oil and Gas Production, Vietsoyepetro J.V., Vietnam*

Oil and gas field development at final stage is accompanied by reservoir energy decrease which involves significant difficulties while drilling in high permeability formation, performing well repair work and stimulating production. This is band up with the technological fluid losses which result in practice shows it is most effective to use in low formation pressure condition the foam system, the stability, density, effective viscosity of which can be controlled using surfactants. However multi-component multiphase foam have not yet been studied well enough to widely apply the foam systems, in oil and gas field practice. In this paper the authors present the result of three-phase foam properties study with different surfactants as well as the instances of foam application. The researches have been conducted on an original unit according to the method worked out by the authors themselves using automatic foam electrical conductivity control equipment. The relations between gas content, stability and effective viscosity values of multi-component foams have been obtained. The results of study serve as a basis for working out the methods of oil and gas well repair as well as the processes of oil and gas production stimulation using foam systems. Instances of applying foam systems during well repair in the oil and gas fields of Russia, Vietnam and Bulgaria are also given.

### **899.K3 CONTROL OF OIL AND GAS FIELD DEVELOPMENT WITH RELAXING DISPERSIVE SYSTEMS, STABILIZED BY SURFACE ACTIVE SUBSTANCES**

**M. Karimov, A. Latypov, A. Odegov, V. Sadykov, F. Tukhbatullin,  
F. Sakhypov, V. Rodin, A. Baranov, R. Mukhutdinov**

*Ufa State Petroleum Technological University, Ufa, Russia, Gas Company "Bashtransgas", Ufa, Russia*

Relaxing dispersive systems stabilized by surface active substances are widely used for intensification of oil and gas recovery from porous formations.

The nature of relaxing dispersive systems depends upon the type of surface active substances and its concentration.

The study shows that the flow behavior of relaxing dispersive systems in a porous medium is a complex one which cannot be correctly described in terms of high apparent viscosity dispersive systems. Also, the concept of relative permeability is not applicable to the flow of relaxing dispersive systems due to the associative nature of its components.

The examination of the processes of dispersive system formation and their areal extent in porous beds show that molecular kinetic factors are fundamental for rheological properties of such systems. The investigations on determination of influence of functional substituents being introduced into dispersed media on kinetic effects in dispersive systems have been conducted. The more preferred functional substituents have been shown from the point of view of their influence on kinetic effects of dispersive systems in porous formations.

A class of surface active substance have been offered which is used for rheological properties control in dispersive systems in the practice of oil and gas recovery from porous formations.

On the base of the results obtained, new technological processes of physical action on formations have been offered with relaxing dispersive systems.

### **900.K3 APPLIANCE OF FOAMING SURFACTANTS IN THE DEVELOPMENT AND EXPLOITATION OF UNDERGROUND GAS STORAGE**

**M. Karimov, A. Latypov, A. Odegov, V. Parfenov, A. Arutujnov, V. Kaigorodov,  
O. Karabelnikov, I. Arbuzov, G. Liberman**

*Ufa State Petroleum Techn. Univ., Ufa, Russia, Joint-Stock Company "Gazprom", Moscow, Russia*

Theoretical and experimental researches of reservoir liquid and gas movement show that surfactants are highly efficient and reliable way of regulating of their fully interchangeability.

There are great importance during the development and cycle utilization of the underground gas storage in reservoirs. Solutions influence study of some surfactants on the main properties of mud, study of their rheological characteristics, the time and degree of mud particles dispersion allowed to develop restoring technology of the gas well productive characteristics after drilling and maintenance overhaul.

Researches of adsorbed foaming properties of surfactants, foam stability, their influence on filtration characteristics of the porous media, on coefficient of reservoir fluids displacement made possible to give some recommendations for calculating optimal concentrations and volumes of surfactants solutions on ways of reservoir treatment to increase its drying degree, forming gas volume in the reservoir, screening reservoir water at the gas withdrawal.

Implementation of the developed procedure has approved that surfactants application reduces the time of putting into service of storage of the water reservoir to cycle exploitation increases gas-saturation of the reservoir, gives rise to forming of gas bubble on less area and provides more steady waterless utilisation of the well at higher output.

New surfactants with predetermined properties opens wide opportunities for utilization of foaming surfactants at the time of the development and exploitation of the underground gas storage.

**901.K3****SURFACTANTS INCREASING THE EFFECTIVE  
OF NATURAL AND ARTIFICIAL LIFT**

**T.S. Phiet, T.L. Dong, Karimov M.F., N.V. Canh**  
*"Vietsovpetro" J.V., Vung tau, Vietnam*

The motion of gas-liquid system in the vertical and incline lift is characterized by regimes: bubble, plug and annular mist. Hydrodynamic friction and fluctuation of pressure in the movement of gas-liquid system are maximum in the plug and annular regime. The theoretical and experimental studies indicate that it is possible prolongation the bubble regime by using surfactants. The surfactants show the influence on the physicochemical properties of oil-gas-water system: slow downs the separation of oil, decreases density of gas-liquid mixture, due to gas is more uniform distribution in the liquid, decreasing relative velocity of gas, decreases fluctuation of pressure. Viscosity of oil-gas-water system decreases due to decomposition of water-oil emulsion. Effectiveness of method is that, for wells have low water cut, due to stabilize the bubble regime in oil phase, a for well has high water cut, due to stabilize bubble regime in water phase. When water-oil ratio changes from 0.3-1.0, it causes to decrease viscosity in the water-oil emulsion. These surfactants are chosen specially for actual conditions in the oil recovery. In this report, authors present the theoretical and experimental results on application surfactants in the increasing the effective of natural flow and artificial lift when lifting oil having high paraffin in the vertical and incline tubing at the oil fields in Vietnam. The received results indicate that, the effectiveness of lifting mixture rises from 20-30%.

**902.K3****DEPOSITION OF AQUEOUS AND NONAQUEOUS BITUMEN  
EMULSIONS IN AN IMPINGING JET CELL**

**R.S. Sanders<sup>1</sup>, R.S. Chow<sup>2</sup>, and J.H. Masliyah<sup>1</sup>**

<sup>1</sup>*Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada*

<sup>2</sup>*Alberta Research Council, Resource Technologies Division, Edmonton, Alberta, Canada*

The oil sands deposits located in northern Alberta provide the largest single source of crude oil in Canada. Over 100 million barrels of synthetic crude oil were produced from the oil sands in 1995.

One of the most serious problems that has arisen in the extraction and processing of bitumen from oil sands is the formation of very stable emulsions. These emulsions are extremely difficult to break and contribute to loss of product, in effectual treatment and disposal of tailings, and even downstream corrosion problems.

A fundamental study of both aqueous and nonaqueous bitumen emulsions was conducted. The impinging jet cell technique and corresponding theoretical model were used to observe and analyze the deposition behavior of bitumen-in-water emulsions and bitumen-stabilized, water-in-hydrocarbon emulsions. Demulsification can be studied using deposition experiments because the droplet-collector interactions observed in deposition experiments are analogous to droplet-droplet interactions that affect demulsification rates. The rate of droplet attachment is dependent upon the nature and magnitude of the droplet-collector interactions that occur as the droplets impinge onto the collector surface.

The effect of droplet concentration, droplet size and surface charge, hydrophobicity of the collector surface, electrolyte concentration and flow intensity on the rates of bitumen droplet deposition will be discussed. Results of the water-in-hydrocarbon deposition experiments, which illustrate the effect of droplet concentration, flow intensity and stabilizing bitumen concentration on the deposition of water droplets suspended in a 4:1 (by volume) mixture of toluene and hexane, will also be presented.

**903.K3 ON THE STABILITY OF WATER IN DILUTED BITUMEN EMULSIONS****X. Wu<sup>1</sup>, T.G.M. van de Ven<sup>2</sup>, and J. Czarnecki<sup>1</sup>**<sup>1</sup>*Synchrude Research Centre, Edmonton, Alberta, Canada*<sup>2</sup>*Department of Chemistry, McGill University, Montreal, Quebec, Canada*

Oil sands deposits in Northern Alberta contain more hydrocarbons than all oil fields of Saudi Arabia. Existing commercial open pit mining operations supply over 15% of Canada's oil production. Oil sand ore typically contains 9-14 wt.% bitumen and about 85% solids, mostly silica sand and a mixture of clays. The bitumen is recovered by a modified flotation method in form of a froth containing about 60% bitumen. The froth is then mixed with naphtha and centrifuged to remove impurities. The centrifuge product, after diluent recovery, is upgraded to synthetic, sweet crude that is shipped out to the market.

The centrifuged diluted bitumen still contains about 3% of water in form of a very stable W/O emulsion with the droplet size of about 3  $\mu\text{m}$ . The emulsified water contains chloride ions posing serious corrosion problems in the down stream upgrading operations. The stabilization mechanism of this emulsion is not yet well understood. Preliminary studies of the trajectories of individual water droplets colliding under shear flow conditions (performed using the so-called colloidal particle scattering method [1]) do not show any long range repulsive interactions between the droplets. This excludes electrostatic or double layer interactions as the possible source of the stabilization.

1. T.G.M. van de Ven, P. Warszynski, X. Wu and T. Dabros, *Langmuir* 10, 3046 (1994).

**904.K3 THE RESEARCH ON CATIONIC POLYMER WATER BASE DRILLING FLUIDS****Liu Yuqing, Piao Changhao, Zhang Keqin***Research Institute of Petroleum Exploration and Development, Beijing, P.R. China*

Cationic polymer drilling fluid (CPDF) is a new water base drilling fluid in which high molecular weight (HMW) cationic polymer (CPAM) is an encapsulation and flocculating agent and organic quaternary ammonium compound (NW-1) acts as shale inhibitor. This paper describes the experimental results of cuttings recovery, particle size distribution layer spacing, and Zeta potential, and discusses the inhibition of CPDF system and its major additives. The advantages of CPDF will be proved by its application in well LX-2

**905.K4 THE THREE-PHASE CONTACT PARAMETERS MEASURING OF THIN WATER FILMS ON MINERAL SURFACES****L. Alexandrova<sup>1</sup> and L. Grigorov<sup>2</sup>**<sup>1</sup>*Institute of Biophysics, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*<sup>2</sup>*Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

The dynamic attachment force is determinant for the flotation effectiveness. The necessary condition for the attachment of the particles to the bubble is the dynamic force to be stronger than the detachment forces at every moment of their interaction. It is known that the dynamic force is very sensitive to the kinetics of rupture of the thin liquid film and the subsequent expansion of the three-phase contact (TPC). Because of that a new method for characterization of the wettability of opaque solid surfaces by measuring a) the lifetime of thin liquid films, b) the kinetics of expansion of TPC, c) the equilibrium contact angle is developed. The technique employed here is essentially based on the microscopy technique developed by Scheludko et al., which enables to observe the TPC on transparent surfaces. The method is proposed for the experimental investigation of the TPC parameters on the opaque solid surfaces.

The important role of the expansion of TPC in the elementary act of froth flotation is experimentally demonstrated for the galena-xanthate systems studied case.

**906.K4****STUDY ON THE SEPARATION OF MAGNESITE FINES  
BY MAGNETIC CARRIER METHODS****Georgios Anastassakis***National Technical University of Athens (N.T.U.A), Athens, Greece*

The production of fine and ultrafine particles during the size reduction or liberation process is inevitable in mineral processing systems and the recovery of the valuable ones is necessary for the improvement of the whole process economics. With the depletion of the high grade ores the problem of the fine particles production and recovery becomes much more intensive.

The processing of the fine and ultrafine particles by the ordinary mineral separation methods, including conventional and column flotation, is inefficient to impossible because of the problems attributed to the small particle size, to their large specific surface area and to their high surface energy.

The carrier methods are included among them developed to separate the fine and ultrafine useful particles from the gangue.

The objective of this paper is to study the feasibility for separating the magnesite fines from the serpentine ones by selective magnetic coating method.

The influence of factors (zeta-potential of the minerals and of the magnetic material, presence of surfactant) which control the selectivity of the process is examined. The total energy of interaction between the particles of the system is calculated theoretically and the conditions which favour the selective magnetic coating are determined.

The experimental results indicate that the separation of magnesite fines from serpentine ones by selective magnetic coating seems feasible and the method holds great promise for further application in the separation of fine and ultrafine mineral particles by controlling the physicochemical factors which influence the selective attachment of the magnetic material.

**907.K4****SYNTHESES OF 4A ZEOLITE IN DETERGENTS WITH KAOLIN****Cao Mingli, Pan Yahong, Yuan Jizu***Dept. of Resources and Envir. Eng., Wuhan Univ. of Tech., 430070, P.R. China*

The main technical conditions for synthesizing 4A zeolite with kaolin were determined. The whiteness and calcium ion exchange capacity (CIEC) of the product were increased by calcining and screening the colouring ions, and the high quality 4A zeolite was synthesized successfully. Moreover, the formation mechanism of zeolite also discussed.

**908.K4****HYDRODYNAMIC AND SURFACE CHEMICAL INTERACTIONS  
BETWEEN BUBBLES AND PARTICLES****Zongfu Dai, Stanislav Dukhin, Daniel Fornasiero, Robert Hayes and John Ralston***Ian Wark Research Institute, University of South Australia, THE LEVELS SA 5095*

The processes by which particles and bubbles interact capture most of the central concepts of colloid science and surface chemistry. This rich and deep area of research involves hydrodynamics, interfacial (including capillary forces), particle and bubble behaviour and solution chemistry. Our work in this area has been both evolutionary and revolutionary, ranging from the preparation of model particle surfaces and the measurement of particle contact angles, to the identification of a flotation "domain", the deformation of a bubble surface upon interaction with a solid surface, the kinetics of three phase contact line expansion, the measurement of attachment efficiencies through to the direct measurement of bubble particle interaction forces. The results, concepts and implications of this work will be discussed, along with our most recent research results dealing with bubble-particle collision models. In this latter case we have developed an experimental and theoretical approach which permits a rigorous test of a collision model where inertial and centrifugal forces are analytically accounted for.

**909.K4****MODEL OF CEMENT RAW MATERIALS PROPORTION  
AND ITS RESOLUTION****Feng Zhongren, Wan Hong, Shi Zhongmin***Dept. of Resources and Environmental Eng.; Wuhan University of Technology, Wuhan, P.R. China*

Cement is a colloidal material with large specific surface area. This paper introduces a model of cement raw materials proportion and its quadratic programming resolution, when three kinds of raw materials are mixed. The calculation of raw materials proportion is quick and easy and the result is reliable. This method is easy to realize on microcomputer. This paper indicates the defects of the least square method and compares them through case study.

**910.K4****A COMPARATIVE STUDY OF COPPER AND LEAD  
ACTIVATION OF SPHALERITE****D. Fornasiero and J. Ralston***Ian Wark Research Institute, University of South Australia, The Levels, S.A. 5095, Australia*

In the flotation of complex sulfide ores, sphalerite often reports to the wrong concentrate. This behaviour has been attributed in part to the activation of sphalerite by copper or lead ions dissolved from chalcopyrite or galena, respectively. In the absence of these metal ions, sphalerite flotation is low with no or little collector adsorption. This inadvertent activation of sphalerite results in a decrease in flotation grade. It is thus imperative to understand this metal activation process and to provide ways of reducing it.

The adsorption of these metal ions on the sphalerite surface has been followed by measuring the changes occurring in solution by Inductively Coupled Plasma emission spectroscopy and on the mineral surface with surface sensitive analytical techniques such as zeta potential measurement and X-ray photoelectron spectroscopy.

The collectorless flotation of sphalerite is high in the presence of lead or copper ions; with increasing pH values, it decreases with lead ions but increases slightly with copper ions. At high copper ion concentrations, sphalerite flotation is depressed between pH 7 and 10 due to the precipitation of copper hydroxide. The increase in flotation is due to the removal of zinc hydroxide and the formation of a sulfur-rich or polysulfide phase at the sphalerite surface. Since the affinity of sulfide ions for lead ions is less than for copper ions, the modification of the sphalerite surface by lead ions is less important than with copper ions. The decrease in sphalerite flotation observed with lead ions at alkaline pH values may be used advantageously in the separation of galena from sphalerite.

**911.K4****OXIDATION OF COPPER SULFIDE MINERALS: A ZETA  
POTENTIAL, XPS AND DISSOLUTION STUDY****D. Fullston, D. Fornasiero and J. Ralston***Ian Wark Research Institute, University of South Australia, The Levels, S.A. 5095, Australia*

Manipulation of the pulp potential has often been used to control the flotation of sulfide minerals in an ore and therefore their separation. Pulp potential affects the oxidation of the mineral surface and the adsorption of collectors. In this study, we compare the ease of oxidation of various copper sulfide minerals including those containing arsenic. The extent of oxidation of these minerals is assessed by monitoring as a function of conditioning gases and time, the changes occurring in solution by Inductively Coupled Plasma emission spectroscopy and on the mineral surface with surface sensitive analytical techniques such as zeta potential measurement and X-ray photoelectron spectroscopy.

The results of this study have indicated the following order for the oxidation of copper minerals:

chalcocite >> tennantite > bornite ≥ enargite ≥ covellite > chalcopyrite

Impurities present on the mineral surface increase the extent of oxidation. The results have major implications for the separation of penalty minerals from their valuable analogues.

## 912.K4 PRECIOUS METALS FLOTATION FROM A COPPER LOW-GRADE ORE

**St. Gaydardjiev**

*Department of Mineral Technologies, University of Mining and Geology, 1100 BG, Sofia*

The possibilities for increased gold recovery by combined processing - flotation and thiourea leaching of gold bearing copper ore from the Bourgas copper deposit are investigated. For the purposes of selective flotation recovery of precious metals - four collectors supplied by Cyanamid company were tested - namely - Aero 412 and 853, Aerophine 3418 and Aerfloat 3477. The best result achieved was with Aero 412. Further on three technological criteria were studied and optimized by the means of regression analysis - pH, degree of milling and collector consumption. The chemistry of each particular collector towards the degree of surface hydrophobization is discussed as well. The final flow sheet proposed encompasses leaching of the remaining tailing product with thiourea in acid media. The main technological factors and relationships for the flotation and hydrometallurgical circuits are graphically represented in a 3D form.

## 913.K4 IMPROVEMENT OF BLEACHING OF KAOLIN USING CHELATING AGENTS

**Gong Wenqi, Wu Xiaohuan**

*Dept. of Resources and Environmental Eng. Wuhan University of Technology, Wuhan, P.R. Chiiza*

Bleaching of the kaolin ore from shaziling kaolin Mine in Jianxi province of China was studied with the aim of enhancing the quality and value of the ore to meet the requirement from the ceramics manufacturers. Factors affecting the reductive bleaching of kaolin ore with sodium dithionite as the bleaching agent were studied and optimized to increase the whiteness of the kaolin ore from 38.5% to about 65%. However, it was found that in the conventional bleaching process, a washing step to remove the ferrous ions from the bleached kaolin suspension was indispensable, which made the process complicated and restricted the capacity of the production. In addition, the whiteness of the bleached kaolin products was unstable. To solve the above problems, a new technique with the application of chelating agents in the bleaching process was developed to remove ferrous ions and get rid of the washing step. The bleaching process of kaolin was simplified. The whiteness of the bleached kaolin products was stabilized as well as increased to about 70%. The mechanism of the bleaching process and the action of the chelating agents were discussed.

## 914.K4 PREFERENTIAL ADSORPTION OF ORGANIC MOLECULES TO SELECTED MINERAL SURFACES

**Rodney G. Harris, John D. Wells and Bruce B. Johnson**

*La Trobe University, Bendigo, Victoria 3552, Australia*

There are many potential applications for systems in which organic molecules adsorb to different extents from aqueous solutions onto disparate solid surfaces. We have been studying in particular the adsorption of a range of polyaromatic and amino compounds onto oxides such as alumina and phyllosilicates such as kaolinite.

Ramaraj *et. al.* (1991) reported that the aromatic dye 3,6-diaminoacridine (proflavin) adsorbs much more strongly to kaolinite than to alumina. Several related compounds (for example Azure A) behave similarly, to the extent that 95% or more of the solute may be removed from solution in the presence of kaolinite under conditions in which less than 5% adsorbs on to alumina. On the other hand there are other compounds which share structural features but which adsorb strongly to both minerals (e.g. Alizarin), or do not adsorb particularly strongly to either one (e.g. Remazol Brilliant Blue R).

One of our objectives is to seek new ways in which water-soluble polymers can be adsorbed selectively to different mineral surfaces. In this paper we will summarise the results of experiments on the selective adsorption of water-soluble organic compounds onto mineral surfaces, comment on structural

features of significance to selective adsorption, and discuss the implications of this work to the selective adsorption of polymers.

R. Ramaraj, D. R. Jeyanthi and C. Srinivasan (1991) *Indian J Chem.* 30A, 1044-1046.

## 915.K4

### EFFECT OF FLOW AND BUBBLE DIAMETER IN THE KINETICS OF FLOTATION OF PYRITE

Eduardo Humeres, Nito A. Debacher and Theodoro M. Wagner

*Departamento de Química, Universidade Federal de Santa Catarina, 88040-900, Florianópolis-SC-Brazil*

The formation of particle-bubble complex in the flotation process depends on the bubble diameter and several mathematical models been proposed to explain this dependency.

In this work is shown the relationship between the flotation rate constant of pyrite and the change of diameter of the nitrogen bubbles obtained by glass plates with porous in the range of 4-250  $\mu\text{m}$ . The kinetics was carried out in a specially modified Hallimond tube that allowed to change the porous plates and controll the gas flow. Pyrite particles had 127  $\mu\text{m}$  mean diameter and for each porosity were obtained the rate constants at three different flows (100, 200 and 300  $\text{ml}\cdot\text{min}^{-1}$ ) at pH 6 (0.05 M succinate buffer) at 25°C. The size of the bubbles does not depend on the porous diameter for porosities in the range of 4 - 160  $\mu\text{m}$ , except for the range of 160-250  $\mu\text{m}$ . The average bubble volume,  $v$ , increases with gas flow, and for porosities in the range of 160 to 4  $\mu\text{m}$  the total bubble concentration stays constant in the volume of confinement of the particles. Consequently, the rate of flotation increases linearly with  $v$  when the gas flow increases from zero to 300  $\text{ml}\cdot\text{min}^{-1}$ .

## 916.K4

### RESEARCH ON EROSION OF SILICON CARBIDE CERAMIC BLADE

Chen Jiayan, Chen Minxiang

*Inst. of Mater. Sci. and Eng., Wuhan University of Technology, Wuhan 430070, China*

Three kinds of silicon carbide ceramic materials were chosen to perform the tests of material erosive wear. The relationship of ambient parameters, abrasive property and target property was studied in these experiments. Some main factors affecting erosive wear rate are determined by analyzing of testing results. A stepwise regression analysis was completed according to the nondimensional quantities obtained by dimensional analysis. Relative hardness (a particle to target  $H_p/H_t$ ) and erosion factor ( $H_p d^{1/2}/K_{tc}$ ) were put forward to evaluate erosion property.

## 917.K4

### METHODS OF SURFACE MODIFICATION OF HIGH DISPERSED FILLERS

Andrzej Krysztafkiewicz

*Institute of Chemical Technology and Engineering, Technical University of Poznan, Poland*

The ability of fillers to reinforcing polymers may controlled by substituting of a hydrophilic surface by a partially or fully hydrophobic one. For this purpose modifying substances are used termed proadhesive compounds. A few techniques are available to change filler particle surface, which leads to improved interaction between polymer and the filler (organophilic transformation). The techniques include change in the type of superficial layer of the filler due to adsorption of modifiers, physical adsorption of a modifying compound to the filler surface (e.g. polymers surface), modification by processing to the filler in solution of proadhesive compounds.



The most convenient way is the latter technique. Filler after surface modification are more difficult to wet with water and demonstrate affinity to non-polar organic fluids. This results in several advantages. Physico-mechanical properties of the polymers become improved (they show greater tensile strength, tearing strength, and they manifest more advantageous values of modules). In this way rubber products are obtained of improved parameters, with the potential of longer exploitation. Moreover, improved processing of the rubber mixture is observed in the technological processes (shorter time of preparation, higher plasticity, facilitated drawing and injection).

For surface modification of high dispersed fillers, various proadhesive, coupling agents and adhesion promoters can be applied. The optimum adhesion promoter for the system including filler and a polymer should couple not only the filler but also polymers. The proadhesive compounds (coupling agents) include silane, titanate, borate, zirconate, hafnate factors, which contain alcoxyl group.

## **918.K4     STUDY ON ULTRAFINE COMMINATION OF HARD KAOLIN AND ITS MECHANISM**

**Lei Shaomin, Cui Guozhi, Zhu Yinbo**

*Non-metallic Mineral Design and Research Institute, Wuhan Univ. of Tech. Wuhan, P.R. China*

The comminution mechanism of hard kaolin from Enshi district in China Hubei province is investigated through applying comminution theory and based on the ore properties of the kaolin. The technique and effectiveness of comminution are introduced according to the practice of ultrafine comminution with an impact comminutor. The results show that the comminutor unit has the merits of being simple technologically, easy to control, high effective and so on.

## **919.K4     THE SELF-GRINDING MECHANISM AND AFFECTING FACTORS OF BULK MATERIAL IN FLUID MOTION**

**Yu Liangzhong**

*Institute of Non-metallic ores, Wuhan University of Technology, Wuhan 430070, China*

The flowability and classification of bulk material (loose body) were introduced, the self-grinding mechanism and affecting factors of bulk materials in various forms of phase, state and motion were investigated. A rotational-flow-state centrifugal autogenous grinder was developed on the basis of applying self-grinding mechanism of bulk material, the result tested by the autogenous grinder was compared with that textured by 4R Raymond mills, fine particles with extremely high specific area were obtained. The feasibility of developed new-type autogenous grinder in the view of fluid motion of bulk material was proved.

## **920.K4     EXPERIMENTAL STUDY ON ULTRAFINE COMMINATION IN THEORY OF VERTIGINOUS CURRENT OF BULK MATERIAL**

**Yu Liangzhong**

*Institute of Non-metallic ores, Wuhan University of Technology, Wuhan 430070, China*

Experiment about ultrafine comminution in theory of vertiginous current of bulk material has successfully performed by a lately developed vertical shaft centrifugal autogenous grinder. The results of several tested materials are analyzed, moreover, the comminution mechanism and the affecting factors of ultrafine comminution are analyzed.

**921.K4 FINE SPECIES INSIDE BOUNDARY LAYERS ON RISING BUBBLES****Elena Mileva, Ljubomir Nikolov***Institute of Physical Chemistry, Bulgarian Academy of Sciences,  
"Acad. G. Bonchev" Str., bl. 11, Sofia 1113, Bulgaria*

The flotation and separation practice show that fine hydrophilic solids are often drawn into the froth product. The aim of the present study is to clarify this phenomenon. The investigation is based on the concept that the particles perturb the boundary layer regions on rising bubbles. It is found that the entities may be divided into three groups: small, medium-sized and large. The first group induces purely viscous disturbance in the background flow, the second gives rise to a prevailing viscous perturbation, and the third - to a gradual transfer towards predominantly inertial interaction. The disturbance velocity and the pressure fields are obtained. The trajectories of the particles inside the layers are calculated for some interesting cases. The basic result is that small and medium-sized particles may be entrapped inside the boundary-layer regions. There exists a realm of solids' dimensions for which this entrainment has a maximum. Besides, the dynamic interactions are different for bubbles with various radii. The optimal region for the detention of the solids for smaller bubbles is  $R_p < R_B / Re_B^{3/2}$ , while for larger bubbles particles with radius  $R_p < R_B / Re_B^{5/4}$  are predominantly captured. It is also shown that the individual interactions of the small species with the boundary layers have important consequences on the collective behavior of groups of mutually non-interacting entities. The proposed model investigations give an interesting possibility for the adequate explanation of the observed entrainment of fine species in many flotation and separation processes.

**922.K4 DIRECT SURFACE FORCE MEASUREMENTS BETWEEN HYDROPHOBIC GLASS SPHERE AND COVELLITE****Rajesh Pazhianur and Roe-Hoan Yoon***Center for Coal and Minerals Processing, Virginia Polytechnic Institute and State University,  
Blacksburg, Virginia 24061, USA*

There is a great deal of interest in direct measurement of surface forces between air bubbles and minerals, which will provide useful information on the nature of wetting films in general and on the process of flotation in particular. However, the measurement is difficult due to the deformation of bubbles. This problem was avoided by substituting the air bubble with a silica sphere hydrophobized by coating the surface with octadecylchlorosilane (ODTCS) so that its contact angles is  $109^\circ$  (Flinn and Yoon 1997). The measurements conducted between the silica sphere and untreated silica plates in dodecylammonium chloride solutions produced the results that are consistent with flotation tests.

In the present work, force measurements were conducted between a covellite (CuS) surface and a hydrophobic glass sphere in the presence of alkylxanthates, which are commonly used for hydrophobizing sulfide minerals. The measurements were conducted as functions of pH,  $E_h$ , reagent concentration, and alkyl chain length. The force curves obtained in the present work can be fitted to the extended DLVO theory, which considers hydrophobic forces in addition to the dispersion and electrostatic forces. It was found that the hydrophobic force increases at  $E_h$  above the reversible potential for the oxidation of xanthate to dixanthogen.

**923.K4 ADSORPTION AND ASSOCIATION PHENOMENA IN SOLVENT EXTRACTION OF METALS****J. Szymanowski***Institute of Chemical Technology and Engineering, Poznan University of Technology, Poznan, Poland*

Hydrophobic extractants having a long alkyl chain(s) bonded directly or via an aromatic ring with a hydrophobic group(s), e.g.,  $SO_3H$ ,  $PO_4H$ ,  $PO_2H$  (phosphinic),  $OH$ ,  $NOH$ ,  $C=O$ , etc., adsorb at hydrocarbon/

water interfaces preparing extractant molecules for complexation with metal species [1]. The same concerns modifier molecules, e.g., hydrophobic alcohols, present in commercial extractants to decrease the extractant complexation power and to increase complex solubility in the hydrocarbon phase. However, modifier molecules compete with extractant molecules in adsorption blocking the interface and decreasing in this way the rate of extraction. Both extractant and modifiers can associate in the hydrocarbon phase forming linear and cyclic associates. Extractants having a strong acidic group, e.g.,  $\text{SO}_3\text{H}$ ,  $\text{PO}_4\text{H}$ ,  $\text{PO}_2\text{H}$ , etc., can also form reversed micelles. The effect of extractant (hydroxyoximes, beta-diketones, pyridine carboxylic acid esters and amides, phosphoric and sulphonic acids, aliphatic and heterocyclic amines) and modifier (alcohols and alkylphenols) structure and the hydrocarbon type on solute adsorption at hydrocarbon/water interfaces, the co-adsorption of two different solutes (two different extractants or an extractant and a modifier) and association and co-association of extractants and modifiers in the hydrocarbon phase are discussed. These phenomena affect both the equilibrium and kinetics of metal extraction which can be modeled when self-association and adsorption of extractant and modifier molecules and their mutual association are taken under consideration. Appropriate procedures are given.

I. J. Szymanowski, *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Boca Raton, 1993, USA.

## 924.K4 BENEFICATION OF COLLOIDAL GOLD FLOTATION USING MACROCYCLES AS MODIFIATORS

Tsarkova<sup>1</sup> L.A., Pertsov<sup>2</sup> N.V.

<sup>1</sup>*Department of Chemistry, Moscow State University, Russia*

<sup>2</sup>*Institute of Biocolloid Chemistry, Kiev, Ukraine*

Foam flotation is the basic method for gold ores recovery. It is known that particles with sizes less than 10 mkm are separated unsatisfactory. The main problem here is the efficiency of fixation of a small particle on a bubble surface, and the following delivery of the particle to the surface. These aspects are well described theoretically.

We consider two experimental possibilities of enhancement of fine particle flotation. Additional technological procedures can be added to conventional flotation:

- selective flocculation by water-soluble polymers into flocs of floatable sizes;
- preliminary aggregation of fine particles using emulsions with selectively adsorbing hydrophobic modifiers.

As selective collectors of gold particles we tested water- and oleo-soluble macrocycles, monomeric or immobilized to polymeric matrixes. As a model system for flotation tests we studied artificial mixture of sand, flotation tails from gold ore and additives of synthetic colloidal gold, modeling free finely dispersed particles.

Low concentrations of gold were determined by atomic absorption technique with extraction emulsion concentration of gold by oil sulfides. Flotation efficiency was studied by variation of concentration, time of agitation and pH of the pulp. 60% recovery of fine gold particles were separated by conventional flotation using polymeric water-soluble azacrownethers as selective flocculants. Mechanism of polymer adsorption was suggested to explain the highest efficiency of flocculant in alkaline medium.

Efficiency of free fine gold flotation was found to be up to 100% in the case of emulsion aggregation. Macrocycles, dissolved in oil-in-water dispersed emulsion, selectively collect gold particles due to chemical adsorption and strong hydrophobization of the surface.

## 925.K4 STUDY OF THE EFFECT OF COAL PYRITE SURFACE OXIDATION ON COAL DESULFURATION BY FLOTATION AND METHODS OF PYRITE DEPRESSION

Shi Xiuping, Zhu Hong

*Department of Coal Preparation and Utilization, CUMT, Xuzhou, 221008, China*

This paper discusses the hydrophobicity of the pyrite surface under different extents of oxidation. Experimental results demonstrate that pyrite is floatable only under initial oxidation of its surface, while the

fresh unoxidized or deeply oxidized surface of pyrite is hydrophilic. In the tests an organic reductant  $C_6H_3(OH)_3$  was chosen as pyrite depressant which is highly efficient, and the sulfur in flotation can be significantly improved.

## 926.K4

### EFFECTS OF RARE EARTH ON METHANE SENSORS' ACTIVATION IN CATALYSIS REACTION

Liu Yongjian, Zhuang Hong, Ou Zechen  
*China University of Mining and Technology*

The partial replacement of the noble metal Pt with rare-earth compound and the application of the compound to the inclusion and modification of traditional methane's catalyst used in oxidation reaction has demonstrated considerable increase both in the absorption of the catalyst and in the activation and stability of the reaction.

## 927.K4

### WHY DOES CHLORELLA "LOVE" GOLD

Yurkova I.N. and Estrela-Llopis V.R.  
*Institute of Bio-Colloid Chemistry, National Academy of Sciences of Ukraine, Kiev*

Experimental investigations of selective heterocoagulation of *Chlorella vulgaris* microalgae and *Bacillus cereus* bacteria with colloidal gold, natural silica and clay particles are used to demonstrate universal method developed by the authors for studies and control of microorganisms aggregation with mineral particles on the basis of notions of extracellular metabolites diffuse layer (EMDL) as a factor playing decisive role on physidal stages of heterocoagulation process.

Influence of two factors has been investigated. Firstly, the selective adsorption of specific groups of extracellular metabolites on mineral particles surface followed with heterocoagulation (neutralization coagulation) of cell and particle, and secondly, role of super long-range action by the mechanism selective diffusiophoresis within the boundaries of EMDL. The universal method is embodied as a complex of interconnected over the phases of culture growth investigations of cell's colloid absorbance of different mineral particles, its electrokinetic potential, quantity of cell ionogenic secretions by conductometry and balance of extracellular metabolites by principal groups. It was established as a result of the studies conducted that extracellular polysaccharides (EPS) are the factor responsible for the selective heterocoagulation of microorganisms with gold.

It was shown that sorption of ionic gold by chlorella is reductive in nature. Regular hexa- and tetragonal flat crystals of gold 3-50  $\mu$  in size have been obtained when chlorella's EPS were utilized as  $Au^{3+}$  to  $Au^0$  reducing agent. So, chlorella 'loves' gold if judged by the nature of the EPS secreted. Methods for intensification of colloid and ionic gold and heavy metals recovery in new technologies of bioflotation, magnetic bioseparation, magnetic and electrobiosorption have been proposed and experimentally developed.

## 928.K4

### THE SURFACE EFFECT IN PROCESSING CHINATONE

Song Zhendong  
*Dept. of Resources and Evor. Eng., Wuhan Univ. of Tech. Wuhan 430070, China*

As one of main raw materials in ceramic industry, chinastone mostly contains minerals such as quartz and sericite. In ultrafine processing of chinastone, the aggregation and adhesion of micropowders caused by surface effect lower the efficiency of ultrafine comminution. A kind of grinding aid for chinastone delaminating has been developed by the author to change the surfacial electronic property of particles and decrease the viscosity of pulp. Experiments about delaminating-comminuting chinastone ores from Nihgcun and shangzhu (Jiangxi Province, China) reveal that the contents of 2  $\mu$ m grade particles are increased from 23% and 27.1% to 42.7% and 45.3% respectively, the products reach the index of first-class chinastone.

## 929.L1 REMOVAL OF EMULSIFIED ORGANICS FROM WASTE WATER FLOWS

G. Angelov

*Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria*

Fine liquid-liquid dispersions are frequently produced in the industry as a result of different processes, manipulations, reactions etc. Their separation is practiced mainly for recovery of valuable products or elimination of pollutants from waste flows. When the droplets are finely dispersed, the emulsion becomes very stable and cannot be easily separated by means of direct phase separation methods, which are based on drop coalescence. Moreover, in the case of partial solubility, the emulsified phase is also dissolved in the flow, and the removal of the emulsion does not mean a complete elimination of the pollution.

An unified approach to the separation of organics finely dispersed and/or dissolved in water flows is the treatment by appropriate solvent. As a result the dispersed fraction (fine droplets) is dissolved and the dissolved fraction is extracted. So the difficult process of the phase separations by coalescence of fine drops is replaced by a process of dissolution of these drops. Following this idea, an apparatus for separation of fine liquid disperse systems through treatment by solvent is designed and its overall performance characteristics are tested. The active part contains a multilayer bed of fibres with selected superficial properties. It is used to facilitate the mass transfer contact destructing the emulsion and extracting the dissolved components. It also promotes the phase consolidation and phase separation processes after the emulsion destruction.

The proposed apparatus can be included in various contacts schemes for multipurpose applications. Schemes with repeated treatment of the waste flow can be used for a deeper removal of the impurities. Contact schemes with multiple solvent recycling are also available. They reduce the solvent quantity in use and its regeneration costs as well.

The apparatus performance is tested on industrial type waste waters containing emulsions of essential oils or harmful organic pollutants.

## 930.L1 SHORT-RANGE ORDER EFFECTS IN THE VIBRATIONAL SPECTRA OF AQUEOUS ELECTROLYTE SOLUTIONS

M.U. Bely<sup>1</sup>, G.I. Gaididei<sup>1</sup>, Yu.B. Gaididei<sup>2</sup>

<sup>1</sup>*Physics Department of Kiev University, 252022, Kiev, Ukraine*

<sup>2</sup>*Bogolyubov Institute for Theoretical Physics, 252 143 Kiev, Ukraine*

Efficient cleaning of water polluted with different harmful impurities is impossible without understanding physical-chemical processes which take place between water molecules and impurity salt ions. It is convenient to study the basic features of these processes using simple molecular anions. Examples are thiocyanates (MSCN) and cyanates (MCNO) which are soluble in water and widely used in technical processes. The purpose of this contribution is to connect the anomalous concentration behavior of the half-band width  $\gamma(c)$  of the stretching vibration (CN) in aqueous solutions of alkali-halide salts with MSCN (MNCO) where M is  $Na^+$ ,  $K^+$ , or  $Cs^+$ ,  $c$  is the alkali-halid salt concentration, with short-range order effects in solutions. It was found that all solutions have a linear dependence of  $\gamma(c)$  but  $\frac{d\gamma(c)}{dc} > 0$  for  $Na^+$  and negative for  $K^+$  and  $Cs^+$ . A theoretical model was proposed and it was obtained that

$$\gamma(c) = \gamma(0) \left( 1 + \frac{1}{2} \left( 10 \frac{q^2 (r_a + r_w)^5}{d^2 (r_a + r_c)^3} - 1 \right) \frac{c}{w} \right),$$

where  $r_{w,a,c}$  is the effective radius of the water molecule, anion and

cation, respectively;  $d(q)$  is the effective dipole moment (charge) of the water molecule (cation),  $w$  is the concentration of water molecules. Thus the interaction between molecular anions and cations gives growing  $\gamma(c)$  but when water molecules can compete with cations for the place near the anion the band width is a decreasing function of the cation concentration.

**931.L1****TREATMENT OF FISHERY INDUSTRY WASTE WATER ARE  
BASED ON USE FLOTATION METHODS****I.G. Beryoza and O.A. Fyodorova***Murmansk State Technical University, Murmansk, Russia*

One of the main problem of the fishery industry waste water is a grease pollution removal.

Nowadays gravitable grease catchers are used for sewage treatment. Work efficiency of this equipment do not exceed 20-25%. The low treatment degree is stipulated physical and chemical properties of the grease pollution:

1. density (appr. 1)
2. great specific gravity of polyunsaturated fat acids (higher hydrophoby).

Aeration is most expedient method of waste water fish grease removal.

Grease catcher pilot plant have been modeled and made. Air have been given in lower pilot plant part though dispersing agent, one are perforated rubber tubes.

Experiments have been conducted in static and dynamic pilot plant work regimes.

Definition of the aeration process optimum technological regime have been carried out method of a experiment mathematical plan. As influencing factors it have been investigated:

- ♦ air giving rate;
- ♦ aeration time;
- ♦ liquid pillar height over dispersing agent.

Efficiency of the grease pollution extraction is about 80 %.

**932.L1****MASS TRANSFER EFFECTS ON THE GROWTH AND BEHAVIOUR  
OF THE BACTERIA *GLUCONOBACTER OXYDANS* ENTRAPPED IN ALGINATE GELS****V. Beschkov, S. Velizarov and T. Georgieva***Institute of Chemical Engineering, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

The biotransformation of glucose to gluconic acid by bacteria of the strain *Gluconobacter oxydans* entrapped in beads of calcium alginate is studied. Experiments under different hydrodynamic conditions (rotary shaker, three-phase bubble column bioreactor) are carried out. The slower biotransformation compared to the free microbial culture due to mass transfer limitations, resulting in the shortage of oxygen and substrate is demonstrated.

An unstructured mathematical model is developed to explain the observed effects. It is shown that for the case of biotransformation strictly associated with bacterial growth the immobilization in gel beads is not appropriate, because of the mass transfer limitations within the particles and therefore the impeded growth of the bacteria.

**933.L1****WATER POLLUTION BY HEAVY METALS  
MICELLAR ENHANCED ULTRAFILTRATION****Françoise Charbit, Annie Steinchen, Cécile Azoug and Gérard Charbit***University of Aix-Marseille, Marseille, France*

Because of the high toxicity of heavy metals, the wastewater's standards are constraining and will become more severe in the near future.

Ultrafiltration (UF) is able to treat large volumes of polluted effluents and we present operating conditions to separate heavy metals from aqueous solutions using ionic micellized surfactants. The separation treatment yields to concentrated solutions and purified water with a composition lying under the standards.

Due to their small size metallic ions pass easily through ultrafiltration membranes ensuring large crossflows. They have to be entrapped to large species to be retained: ionic surfactants micelles<sup>1</sup> are suitable complexing agents for the required depollution treatment. For the above-mentioned ions effluents containing

500 times the cadmium standard and 200 times the hexavalent chromium standard are purified by a single UF stage and less than 20 mol/m<sup>3</sup> as surfactant concentrations. The same process is efficient to treat effluents containing ions mixtures: Cd<sup>2+</sup>, Cr(VI), Ni<sup>2+</sup>...

The influence of organic compounds (alcohols, acids, ...) and salts in the feed is experimentally studied. Indeed, the micellar enhanced ultrafiltration process (MEUF) is flexible and rather large ranges of operating conditions are open for an efficient separation performed either continuously or in batch conditions.

In addition to these technological experiments we have built up a model in order to rationalise the results of retention of the micelles based on the thermodynamics of their reversible processes (TIP). In this approach, the membrane containing the permeants is considered globally as a liquid phase. Applying to this solution the TIP approach, we obtain by means of some non restrictive assumptions the value of the cross flow. It depends explicitly on the interactions between the permeants and the membrane material and between the permeants among themselves. This model is consistent with the very classical model of the resistances in series. It gives in addition new insights in the interactions involved in the different parts of the experimental resistances and it explains their variations against the variations of the feed solutions. It could be as well applied to other systems (other membranes and other feed mixtures).

<sup>1</sup>sodium dodecylsulfate (NADS) and cethyltrimethylammonium bromide (CTABr) are used to separate respectively the cadmium (Cd<sup>2+</sup>) and hexavalent chromium (CrO<sub>4</sub><sup>2-</sup>) ions from aqueous solutions.

### 934.L1 EFFECT OF BIOSURFACTANTS PRODUCED BY HYDROCARBON- OXIDIZING BACTERIA ON BIOREMEDIATION OF OIL-POLLUTED SOIL AND WATER

Chugunov V.A., Jigletsova S.K., Mironova R.I., Rasulova G.E., Martovetskaya I.I., Kholodenko V.P.  
*State Research Center for Applied Microbiology, Moscow region, Obolensk, Russia*

Synthetic and biological surfactants are rather promising to be used for cleanup of discharged water, aquatic areas and soil polluted with petroleum and its by-products. This may be due to hydrocarbons solubilization that makes them more accessible to chemicals and oil-oxidizing microorganisms. Many oil-degrading microorganisms are known to produce emulsifying agents. 30 oil-degrading strains of 5 genera were quantitated by means of different tests (measurement of contact angle, hexadecane emulsification and others). All strains were studied in respect to their ability to produce extracellular surfactants. The strains studied were found to vary significantly in their bioemulsifying activity. Upon cultivating strains in liquid media, no steady correlation between their abilities to produce emulsifiers and to utilize oil was observed. Surfactants were isolated from a culture liquid by conventional methods and their effect on the extent of cleanup of oil-polluted soil and water was studied. It has been found that oil utilization by indigenous microflora of gray forest soil was greatly enhanced (up two-fold) in the presence of bioemulsifiers added in, various concentrations. The extent of oil biodegradation with a crude bioemulsifier added (2 mg/g) was 30% for a month. The same effect was observed for inoculated cells of the active bioemulsifying and oil-oxidizing strain of *Rhodococcus* (10<sup>7</sup> cells/g). Similar results were obtained upon treating oil-polluted water samples. It can be concluded that environmentally safe and rather cheap biosurfactants or bioemulsifying microorganisms can be successfully employed for stimulated hydrocarbon biodegradation. Research has been performed in the framework of Project 119-95, ISTC.

### 935.L1 NATURAL ORGANIC MATTER FOULING OF NANOFILTRATION MEMBRANES

Menachem Elimelech and Seungkwan Hong  
*Department of Civil and Environmental Engineering School of Engineering and Applied Science,  
University of California, Los Angeles, CA 90095-1593, USA*

The role of chemical and physical interactions in natural organic matter (NOM) fouling of nanofiltration membranes is systematically investigated. Results of fouling experiments with three humic acids demonstrate that membrane fouling increases with increasing electrolyte (NaCl) concentration, decreasing solution pH, and addition of divalent cations (Ca<sup>2+</sup>). At fixed solution ionic strength, the presence

of calcium ions, at concentrations typical of those found in natural waters, has a marked effect on membrane fouling. Divalent cations specifically interact with humic carboxyl functional groups, and thus, substantially reduce humic charge and the electrostatic repulsion between humic macromolecules. Reduced NOM interchain repulsion results in increased NOM deposition on the membrane surface and formation of a densely packed fouling layer. In addition to chemical effects, results show that NOM fouling rate increases substantially with increasing initial permeation rate. It is demonstrated that the rate of fouling is controlled by an interplay between permeation drag and electrostatic double layer repulsion; that is, NOM fouling of NF membranes involves coupling between physical and chemical interactions. The addition of a strong chelating agent (EDTA) to feed water reduces NOM fouling significantly by removing free and NOM-complexed calcium ions. EDTA treatment of NOM-fouled membranes also improves the cleaning efficiency dramatically by disrupting the fouling layer structure through a ligand exchange reaction between EDTA and NOM-calcium complexes.

**936.L1****INTEGRAL TOXICITY BIOTESTING USING WATER  
POLLUTED WITH FUELS**

**Fomchenkov V.M., Irkhina I.A., Novikov I.A., Kholodenko V.P.**

*State Research Center for Applied Microbiology, Moscow region, Obolensk, Russia*

Development of the civilisation has created undesirable anthropogenic pollution of the environment. At present, the problem of protection of the environment against different pollutants, in particular against fuels, is considered to be the "hottest". However, it is impossible to choose an effective protection strategy without having reliable data on the status of the environment. Different methods are used for assessment of the environment. Biological assays have certain advantages compared to others. They respond to the total effect of all available toxicants and indicate integral toxicity of any object under research. In our experiments different bioassays based on physiological, biochemical and biophysical indices of microbial test organisms were studied. These were electro-orientational spectroscopy, osmo-optical method, bioluminescence assay, dye colour reaction test and a growth test on microorganisms. The methods were tested using water samples polluted with fuels. The disturbance of barrier properties of cellular membrane after pollutant treatments has been shown by means of electro-orientational spectroscopy and osmo-optical methods. A 20% decrease in luminescence of *Photobacterium leiognathi* BKM B-1719 was found in water samples polluted with 0.001% diesel fuel and petrol as well as in samples with 0.03% oil. 14 bacterial test-cultures were used in experiments with 1% kerosene polluted samples. Test-cultures such as *Agrobacterium radiobacter* BKM B-1218, *Escherichia coli* B824 and K-12, *Bacillus pasteurii* and *Pseudomonas stutzeri* BKM B-903 were found to be the most sensitive. Integral toxicity was assessed after destructing the pollutant using the dye colour reaction test on cells of *Agrobacterium radiobacter*. In water samples polluted with 10% diesel fuel there was recorded a decrease in integral toxicity after treating samples with 5-day incubated association of cells of three destructing strains. Results suggest that all above mentioned bioassays are very promising both for assessment of integral toxicity of polluted water and monitoring the process of bioremediation of polluted sites. Research has been performed within the framework of Project 119-95, ISTR.

**937.L1****ELECTRO-ORIENTATIONAL STUDY ON THE EFFECT  
OF CATAMINE AB AND TRIBUTYLTHINCHLORIDE ON BACTERIAL  
CELLS INDUCING CORROSION OF METALS**

**Fomchenkov V.M., Kobelev V.S., Akimova N.A., Kholodenko V.P.**

*State Research Center for Applied Microbiology, Moscow region, Obolensk, Russia*

Microbially induced metal corrosion is known to be responsible for pronounced environmentally hazardous accidents. At present, applying of biocides is considered to be one of the widely accepted corrosion abatement methods. In this connection, of considerable importance is understanding of mechanisms underlying the harmful effect produced by biocides and their mixtures on corrosion-inducing microorganisms. Electro-orientational spectroscopy makes it possible of detecting changes of properties inside of cells as well as on their surfaces. Bacterial cells of two strains were used in our studies. All cells



were isolated from corroded metallic objects and analysed for their response to catamine AB and tributyltin-chloride (TBTC). EO-spectra obtained were examined. It has been found that properties of the cell surface are undergone a change. This indicates the fact that adsorption of biocidal molecules takes place on its surface. Moreover, significant variations within a high frequency region of the spectrum were recorded that bear witness to the disturbance of barrier properties of cell membranes. Combinations of catamine AB and TBTC were found to be the most effective, especially when used at concentrations of 0.001% and 0.002%, respectively. Results suggest that the biocides interact efficiently with the cell surface resulting thus in the disturbance of barrier properties of cell membranes. The biocides are very much effective if used in combination. Research has been performed within the framework of Project 119-95, ISTC.

### 938.L1 LOW FREQUENCY SONO- ELECTROCOAGULATION OF IRON HYDROXIDES

V. Kovacheva-Ninova, M. Parlapanski

*University of Mining and Geology, Sofia, Bulgaria*

As it is well known a number of methods for purification of waste water are used at present. They may be physical, chemical, biotechnological, biophysical, biochemical and electrochemical ones. One of the methods associated to the last group (electrochemical methods) represents the process of electrocoagulation implemented in waste water. In fact, it may be defined as a process of transformation of colloidal phases containing in the water to rough-dispersion phases and their following coagulation and sedimentation. With the sediment a part of ion- molecular and solid contaminations are removed from the water.

On the other hand, the action of ultrasound upon the electrochemical processes has been an object of an on going investigations. It is established that the treatment of the electrolyte in a given electrolytic cell by an ultrasound improves significantly the kinetics of the electrode processes. It should be noted, however that previous investigations of the authors have shown that the ultrasound may be replaced successfully by an acoustic low frequency field. In order to investigate the influence of sonic treatment with a low frequency upon the process of electrochemical obtaining of colloidal iron oxides an effective combined sono-electrochemical appliance was constructed. By using this instrument a series of experiments were accomplished involving a combined sono-electrochemical treatment of solutions of NaCl and ZnSO<sub>4</sub>. It was established that the use of low-frequency sound at different conditions (amplitude and frequency) increase the quantity of obtained colloidal sediment of iron hydroxides with 20%-44% for solutions of Cl<sup>-</sup> and with 11%- 62% for solutions of SO<sub>4</sub><sup>2-</sup>.

### 939.L1 ULTRADISPERSED DIAMONDS ACTION ON BACTERIAL BIOLUMINESCENT REACTION

Kratasyuk V.A., Kudryasheva N.S., Belobrov P.I.

*Institute of Biophysics, Krasnoyarsk, Russia*

Ultradispersed diamonds (UDD) action on enzymatic processes results in negative effects on human organism. Bacterial bioluminescence system *Photobacterium leiognathi* has been chosen as model for studying UDD action on enzymatic reactions. Typical human organism enzymatic processes (respiration, hydrocarbons exchange, hydroxylation, dealing with migration of energy, electron, hydrogen, etc.) are similar to those for bioluminescent system too. Ultradispersed diamonds (UDD) action on enzymatic processes results in bacterial bioluminescent systems as a model of enzymatic reaction was studied. Changes of bioluminescence kinetics in UDD presence were described. UDD's quenching efficiency dependence on bioluminescent components (enzymes, FMN, aldehyde, NADH) concentrations and physical factors of bioluminescent solution (pH and ionic force) was studied. One of possible mechanism of bioluminescence quenching - energy migration - was discussed. Absorption spectra of UDD dilute water slurries were described.

**940.L1****EFFECTS OF THE CHEMICAL SUBSTANCES  
ON THE IMMOBILIZED BIOLUMINESCENT SYSTEM****Kudryasheva N.S.***Institute of Biophysics, Krasnoyarsk, Russia*

Biotests based on the bacterial bioluminescence are widely used in ecology monitoring. Showing the integral toxicity of an ecology object they are cheap, rapid and sensitive. The new worth-while direction of bioluminescent biotesting is the creation of the test-systems immobilized in starch gel. They are stable, sensitive, handy in use and keeping. The possibility to use the coupled enzyme bioluminescent system NADH:FMN-oxidoreductase bacterial luciferase immobilized in starch gel for ecology monitoring of water systems was investigated. Its sensitivity to the model solutions of inorganic and organic compounds is of grate interest. The effects of the rows of metallic salts and organic compounds were studied. The inhibition and activation constants of the compounds were calculated. The differences in the constants were connected with electronic structure of the compounds - nature of their external orbitals, charges, radii of the cations, energy of the electron-excited states, aromatic, and aliphatic part-size of the aromatic molecules etc. The effects were compared to these for the two other bioluminescent systems-luminescent bacteria and water soluble coupled enzyme bioluminescent system NADH:FMN-oxidoreductase - bacterial luciferase. Differences in effects have been explained with the diffusion rate, rule the cellular shell and the respiration effects of bacteria. The results can be used for choosing of the more sensitive system in the monitoring of the definite pollutants.

**941.L1****THE PURIFICATION OF PROTEIN BY  
SURFACTANT-PRECIPITATION METHOD****Xue-gang Li, Jia-li Dong***Southwest Agricultural University, Centre Laboratory, Chong Quing 630716, China*

The protein can be precipitated from solution when it combines with surfactant in some case [G.-X. Zhang, X.-G. Li, X.-H. Huang, J.-L. Dong (1996) *Acta Biophysica Sinica*; 12: 187], which may be used to purify and separate protein.

**942.L1****MONITORING OF NON-IONIC SURFACTANTS ADSORBED  
ON PARTICLES OF RIVER WATER (WARTA RIVER POZNAN)  
OVER THE PERIOD OF AUGUST 1994 TO OCTOBER 1996****Zenon Lukaszewski, Andrzej Szymanski and Bogdan Wyrwas***Technical University of Poznan, Institute of Chemistry, Poznan, Poland*

Although the determination of non-ionic surfactants (NS) adsorbed on particles of river water is a difficult problem, it has been successfully solved [1]. Two different methods have been developed for this purpose: direct extraction of NS from particles separated by filtration and the difference approach, where concentration of adsorbed NS is calculated from the difference between the total concentration of NS in river water (i.e. both dissolved as well as adsorbed on particles) and the concentration of dissolved NS. The indirect tensammetric measurement is used for final determination of NS in both cases.

These methods were applied for monitoring NS adsorbed on particles of river water of Warta River in Poznan over the period of August 1994 to October 1996. Annual average concentrations of NS dissolved in water of Warta River, at the place of sampling, were  $42 \mu\text{g l}^{-1}$  for 1994,  $57 \mu\text{g l}^{-1}$  for 1995 and  $81.5 \mu\text{g l}^{-1}$  for 1996. Average concentration of particles in the tested river water was approximately constant over the period of testing ( $42 \mu\text{g l}^{-1}$ ), although big variation between single measurements were recorded (from 15 to  $76 \mu\text{g l}^{-1}$ ).

Average concentration of NS adsorbed on particles of river water over the period of testing was  $13.3 \mu\text{g l}^{-1}$  as determined directly and  $11.5 \mu\text{g l}^{-1}$  as determined by the difference approach. Higher value

corresponds to average flux of NS adsorbed on particles equal 18.5 % of total flux of NS. Annual concentration of NS adsorbed on particles was  $11 \mu\text{g l}^{-1}$  for 1994,  $12.7 \mu\text{g l}^{-1}$  for 1995 and  $14.6 \mu\text{g l}^{-1}$  for 1996 (as determined directly). These values correspond to annual average flux of NS adsorbed on particles equal 22.7% of total flux for 1994, 18.7% for 1995 and 17.0% for 1996.

The observed picture may be explained by growing annual average concentration of NS and by roughly constant flux of particles.

1. B. Wyrwas, A. Szymanski and Z. Lukaszewski, *Anal. Chim. Acta*, 331 (1996) 131

### 943.L1      **INDIRECT TENSAMMETRIC TECHNIQUE: A POWERFUL TOOL FOR MONITORING OF NON-IONIC SURFACTANTS AND THEIR METABOLITES IN THE AQUATIC ENVIRONMENT**

**Zenon Lukaszewski, Andrzej Szymanski and Bogdan Wyrwas**

*Technical University of Poznan, Institute of Chemistry, Poznan, Poland*

Currently the BiAS and CTAS methods are recommended for the determination of non-ionic surfactants (NS) in the aquatic environment. These methods are cumbersome and time-consuming. They are characterised by very poor precision and the detection limit of 50 -100  $\mu\text{g}$  of NS in the sample. The indirect tensammetric technique (ITT) applied with adequate separation scheme offers much better detection limit (1.5  $\mu\text{g}$ ) and precision (expressed as RSD) below 0.1 [1]. The ITT may be flexibly applied in numerous environmental problems, not solved yet.

Tensammetry belongs to the group of voltammetric methods. However, in contrast to the majority of voltammetric techniques, double layer capacity changes are measured in tensammetry. Instead of direct measurement, the lowering of tensammetric peak of monitoring substance due to competitive adsorption of NS is the analytical signal in the ITT. The monitoring substance usually used is ethyl acetate, showing single well shaped tensammetric peak. This signal is tolerant to anionic surfactants and reacts additively to different NS. Therefore the total concentration of NS can be easily measured. The ITT was applied in combination with an extractive separation scheme (the indirect tensammetric method - ITM) as well as in combination with the BIAS separation scheme (BiAS-ITM) [2]. Simultaneous determination of NS and poly(ethylene glycols) (PEG) is possible in the ITM. Simple extraction with ethyl acetate ensures separation of NS from water matrix. Consecutive extraction with chloroform separates PEG from the same sample. Then NS are determined in ethylacetate extract while PEG, in chloroform extract. The ITM was applied for monitoring NS and PEG in influents, processing liquors and effluents of numerous sewage treatment plants. Apart from efficiency of removal of NS in tested plants, the level of PEG was determined. PEG were present in all tested plants and their concentration in the effluents was usually higher than residual concentration of NS. The ITM was also applied for monitoring of NS and PEG in river water over six years. Long term trends in, NS concentration as well as seasonal changes of concentration were apparent. PEG were present in every tested sample, River water die-away test of 'native' NS of river water was easily monitored using the ITM. This kind of measurement may be used as a test of biodegradative power of river water.

The BiAS-ITM was applied for monitoring of NS adsorbed on particles of river water. Approximately 20 % of total flux of NS in river water was transported in the form over the period of testing. Modified version of BIAS-ITM was used for the determination of NS in the presence of excess of petroleum products. The method shows good precision and recovery. Both ITM and BiAS-ITM were applied for measuring primary biodegradation in NS tests especially under conditions of the OECD Confirmatory Test. Apart from NS also PEG as metabolites of biodegradation of oxyethylated alcohols were measured during this test. It was distinctly shown that PEG are the major intermediate product of biodegradation of this group of NS.

1. A. Szymanski, B. Wyrwas and Z. Lukaszewski, *Anal. Chim. Acta*, 305 (1995) 256

2. B. Wyrwas, A. Szymanski and Z. Lukaszewski, *Talanta*, 42 (1995) 1251

## 944.L1 POLY(ETHYLENE GLYCOLS) AS METABOLITES OF NON-IONIC SURFACTANTS BIODEGRADATION IN THE AQUATIC ENVIRONMENT

Zenon Lukaszewski, Andrzej Szymanski and Bogdan Wyrwas  
*Technical University of Poznan, Institute of Chemistry, Poznan, Poland*

Poly(ethylene glycols) (PEG) are major metabolite product of biodegradation of non-ionic surfactants (NS). PEG are formed according to "central fission pathway". Two alternative pathways are also reported in the literature. The knowledge concerning PEG in the aquatic environment is scanty and scattered. The reason may be a lack of sufficiently effective analytical methods. Recently two very effective methods have been developed for this purpose: the indirect tensammetric method (ITM) [1] and the method combining the BiAS separation scheme with the indirect tensammetric measurement (BiAS-ITM) [2]. The ITM may be used for measuring total concentration of PEG while more selective BiAS-ITM, for concentration of PEG having more than 4 oxyethylene subunits. Consecutive extraction of water sample with ethyl acetate and chloroform has been applied both in the ITM and BiAS-ITM. Its aim is separation of PEG from water phase and from NS. PEG are gathered in the chloroform phase. The BiAS-ITM, as more selective than the ITM, uses selective precipitation of compounds having oxyethylene chain with Dragendorff reagent. However, only those having more than 4 oxyethylene subunits are precipitated. The difference of the ITM and BiAS-ITM may serve as a measure of concentration of a fraction of PEG having 1-4 oxyethylene subunits. The separation of this fraction and independent measurement of its concentration is also possible.

These methods were applied for investigation of different kind samples of aquatic environment: influents and effluents of sewage treatment plants and river water as well as in testing of biodegradability of NS under conditions of the OECD Confirmatory Test and the river water die-away test. In ten investigated sewage treatment plants, considerable concentration of PEG was found in all instances both in the influents as well as in the effluents. In the case of the effluents, the PEG concentration was much higher than residual concentration of NS. Considering PEG as metabolites of NS biodegradation may explain this fact. PEG are commonly present in river water monitored at Warta River in Poznan over the whole year. Their average concentration were as high as 40 % of average total stream of NS. PEG appeared to be a major product of biodegradation of „native” NS of river water from Vistula River in Cracow as well as a major metabolite of biodegradation of oxyethylated alcohols tested under conditions of the OECD Confirmatory Test. During the initial period of the test long chain PEG were major intermediate products of biodegradation. However, after a few days short-chain PEG predominated in the effluent. Very probable reason of this effect is gradual adaptation of micro-organisms of activated sludge to PEG. A common presence of PEG in samples of the aquatic environment is argument supporting the central fission pathway of biodegradation of NS.

1. A. Szymanski, B. Wyrwas and Z. Lukaszewski, *Anal. Chim. Acta*, 305 (1995) 256
2. B. Wyrwas, A. Szymanski and Z. Lukaszewski, *Talanta*, 42 (1995) 1251

## 945.L1 SURFACTANTS IN PROVIDING ECOLOGICALLY SAFE PROCESSES

Panaeva S.A., Maljutin S.A.

*NPAO "SintezPAV", Joint Stock Company, "Shebekino Chemical Factory", Shebekino, Russia*

The use of aqueous solutions of polyfunctional surfactants (PS) is proposed as one of the ways to resolve the ecological and energy crisis in existing technologies in stages where aggressive media are used.

In microelectronics it is necessary to clean the silicium plates (or A B structures) from metal ions prior to all thermal operations when making p-n junctions which requires large quantities of extra pure mineral acids. The replacement of the acids by aqueous PS solutions allowed not only to lower the consumption of the acids and to solve many ecological problems, but also to increase the yield of useful articles. (This development was awarded a gold medal at the World Exhibition "Brussels -Eureka 95").

For plating manufactures, where acids are also used in large quantities, "depressates" for chroming baths "TNS 16-20" and preparations of the series "ME-4" were developed, aqueous solutions of which replace acids in etching baths prior to plating. Our potentials of making new PS-based compositions replacing aggressive media are unlimited since our investigations aimed at making them are based on known but unasked-for knowledges of discovered co-operative systems leading to the formation of self-organized

dissipative structures. Discussed are action mechanisms of aqueous solutions of preparations in solution-surface contact.

### 946.L1 APPLICATION OF THE HETEROGENEOUS HYDROLYSIS FOR THE RECOVERY OF METALS FROM COMPLEXING MEDIA AND THE INDUSTRIAL WASTE WATER TREATMENT FROM NON-FERROUS METALS

S.I. Pechenyuk

*Kola Science Centre of RAS, Institute of Chemistry, Apatity, Russia*

The principles of approaching the selection of the metals recovery conditions from the complexing media have been found. The high sorptional recovery of metals from these media is possible only under the condition when a fast and deep transformation of the sorbat in the sorbent phase takes place. The heterogeneous hydrolysis guarantees this condition. The effective metal recovery from a complexing medium is possible, if  $\lg K_{st} < 40$  ( $K_{st}$  - the stability constant of the metal complex in the given medium). From the practical point of view, the reasonable time of recovery is achieved when the ligand half-exchange time of the given complex is equal to 2-3 days at 20-100°C. As sorbents iron or zirconium gelatinous oxyhydroxides or crystalline oxyhydroxides of rare earth elements (REE) with  $pH_{pzc} > 6.5$  ( $pzc$ - point of a zero charge) can be used. For the recovery of metals forming labile but thermodynamically stable complexes (Pt, Pd, Ni) neutral or weak-basic gelatinous sorbents should be used. For the systems with low ligand concentrations or inert complexes (Ir, Cr) in the salt media the crystalline REE oxyhydroxides should better be used. These principles were supported by different tests carried out on technological solutions, i.e. the recovery of Ir from copper-nickel solutions, Pt from  $NaCl + NaClO_4$ -media, the treatment of industrial waste waters from Cr, Cu, Ni, Pb, Mn, Zn. This method is applicable for technological and analytical purposes, is cheap and easy.

### 947.L1 COLLOID-CHEMICAL PROPERTIES OF TWEEN-80 - EXCELLENT NONIONIC SURFACTANT FOR WATER DECONTAMINATION

M.V. Poteshnova, N.M. Zadymova, Z.N. Markina

*Department of Chemistry, Moscow Lomonosov State University, Moscow, Russia*

Pollution of water by toxic and hazardous organic pollutants is an environmental concern. Hydrophobic organic compounds, such as aromatic hydrocarbons (for example toluene), are of special interest because their own solubility in water ( $S_w$ ) are greater than their limiting allowable concentration (LAC). The addition of suitable amphiphiles to aqueous wastes can be exploited for decontamination purposes. In the presence of micelles, organic pollutants bound to these aggregates can be removed using colloid-chemical methods. Surfactants of various types were investigated: cationic, anionic and nonionic. Nonionic surfactant Tween-80 proved the best because it is able to solubilize relatively great quantities of toluene (7,6 mole toluene per mole micellar surfactant at 293K, in contrast to sodium dodecyl sulphate - 0.5 mole toluene per mole micellar surfactant). Besides Tween-80 is not toxic, is biodegradable and therefore environmentally safe. The purposes of these study are: (1) to determine colloid-chemical properties of aqueous Tween-80 solutions at different temperatures, (2) to develop laboratory technique for water purification from model pollutant (toluene) up to LAC. The effect of temperature on the surface activity ( $J$ ), and calculated thermodynamic functions of adsorption ( $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ ) was studied using systematic precision ( $\pm 0.02$  mN/m) measurements of the surface tensions  $\sigma$  for aqueous solutions of Tween-80 in wide range of concentration under adsorption equilibrium at 293-333K. The presence of micelles with an aggregation number  $n=32$  in aqueous Tween-80 solution at 293K was demonstrated on the basis of precision tensiometric data in CMC region and method suggested by Rusanov. Equilibrium solubility of toluene in aqueous solution of Tween-80 was determined by refractometric technique at 293-303K. Solubilization of toluene commenced at the surfactant critical micelle concentration (CMC) and was proportional to the concentration of surfactant micelle form. Values of molar solubilization ratio (MSR), micelle-phase/aqueous-phase partition coefficient  $K_m$  and changes of Gibbs free energy ( $\Delta G_T^0$ ) of solubilization were calculated. It was shown that at increasing temperature MSR increases from 7,6 to 9,8 mole toluene per mole micellar

surfactant. At the same time  $K_m$  and  $\Delta G_T^0$  decrease ( $\ln K_{m,293K}=8,93$ ,  $\ln K_{m,303K}=8,86$ ;  $\Delta G_{293K}^0=-21,8$  kJ/mole,  $\Delta G_{303K}^0=-22,3$  kJ/mole). We suggest that unusually great value of MSR is due to the fact that toluene is concentrated in polyoxyethylene palisade layer, but not only in hydrophobic core micelle. Solubilization and foam separation techniques using Tween-80 have been developed to remove toluene ( $C=0.094$  mole/l) from water up to LAC.

**948.L1****THE DISTRIBUTION OF STRONTIUM IONS DURING THE TRANSFORMATION OF AMORPHOUS CALCIUM PHOSPHATE TO CRYSTALLINE HYDROXYAPATITE AT AN ELEVATED pH**

Raicevic S.<sup>1</sup>, Lizunova T.L.<sup>2</sup> and Komarov V.F.<sup>2</sup>

<sup>1</sup>Radiation and Environmental Protection Department, Institute of Nuclear Sciences "Vinca",

P.O.Box 522, 11001 Belgrade, Serbia, Yugoslavia

<sup>2</sup>Chemical Department, Moscow State University, Moscow 11734, Russia

Phosphate precipitation is one of the frequently used methods for the removal of radioactive strontium and other pollutants, such as heavy metals or phosphates, from wastewater. However, for the optimization of the existing treatment processes or the implementation of a new one it is useful to investigate: a) physico-chemical characteristics of a precipitate, b) mechanism of phase transformation and c) interaction of impurity with different solid phases. In this paper, the interaction of strontium with precipitated calcium phosphates which leads to the isomorphous substitution of strontium ions with calcium ions, was investigated.

Calcium phosphates were precipitated from calcium nitrate and potassium phosphate solutions at pH=10.8 and 20°C. The ratio of Ca/P = 1.67 in the initial solution corresponds to the stoichiometric composition of HA. The pH was maintained at 10.8 by the addition of potassium hydroxide. The first phase obtained is metastable amorphous calcium phosphate [ACP,  $Ca_3(PO_4)_2$ ] which is transformed after the induction period into stable crystalline hydroxyapatite [HA,  $Ca_{10}(PO_4)_6(OH)_2$ ]. Structural and morphological analysis of the precipitated solid phase were previously performed by x-ray powder diffraction, transmission electron microscopy and specific surface area measurements. The kinetics of transformation, using solutions labeled with <sup>45</sup>Ca and <sup>32</sup>P, was determined radiometrically. In the same experimental conditions a strontium nitrate solution, labeled with <sup>85</sup>Sr was added in the synthesis together with a calcium ion. The composition of the solid phase was calculated on the basis of the material balance equation. The results have shown that ACP→HA transformation is completed in about 650 minutes. The relation between the level of transformation and distribution coefficients of <sup>85</sup>Sr has been established.

Distribution coefficients of strontium ions between liquid phase and solid ACP or HA phases were:  $D_1=(0.41\pm0.02)$  and  $D_2=(0.20\pm0.02)$ , respectively. Based on the obtained distribution coefficients it could be concluded that, under these experimental conditions, strontium ions are preferentially located at structurally distinct  $Ca_{II}$  sites in the crystal lattice of HA.

**949.L1****STABILITY FACTORS AND ENVIRONMENTAL ROLE OF SUSPENDED PARTICLES IN NATURAL WATERS**

I. Sondi, N. Vdovic, and V. Pravdic

Center for Marine Research, "Ruder Boskovic" Institute, Zagreb, Croatia

Suspended mineral matter, consisting of colloiddally stable particles, is one of the key elements of natural waters: it carries biogenic elements, organic detrital matter, and inorganic and organic pollutants from land to sea. Studies are reported on two model clay minerals beidellite and ripidolite, two commercially available calcites, and silica. The influence of mechanical surface modification by particle size reduction, a process of weathering and disintegration in natural aquatic media, the influence of ionic strength, and of the adsorption of organics is reported. Stable particles interact with solutes providing adsorbing surfaces characterized by mineral composition, organic coating, some with large specific surface areas, electric charge, and as surfaces for specific adsorption of large organic molecules and polymers. A case is reported on investigations of river transport to the Adriatic sea. The discussion is centered on the role of particles in

the self purification capacity of natural waters, and in the estimate of the contribution of suspended particles in determining the ultimate receiving capacity for waste producing human activities in the riverine watershed area.

## 950.L1 MICELLAR CATALYZED REACTION OF A PHOSPHATE ESTER: EFFECT OF THE DIELECTRIC CONSTANT OF THE MEDIUM

Elizabeth Fátima de Souza<sup>1</sup> and Lavinel G. Ionescu<sup>2\*</sup>

<sup>1</sup>Instituto de Ciências Biológicas e Química-Pontifícia Universidade Católica de Campinas -  
PUCCAMP, Campinas - SP, Brazil

<sup>2</sup>Departamento de Química, CCNE, Universidade Luterana do Brasil - ULBRA, Canoas-RS, Brazil &  
Instituto de Química, Pontifícia Universidade Católica do Rio Grande do Sul-PUCRS,  
Porto Alegre -RS, Brazil

Phosphate esters are compounds with interesting biochemical and pharmacological properties and are widely used as drugs, pesticides and nerve gases. Their accumulation and their effect in the environment are of paramount importance. In previous studies, reported in literature, we have shown that the alkaline hydrolysis of di- and tri-substituted phosphate esters is catalyzed by various surfactants and is also affected by the addition of dimethyl sulfoxide to the reaction medium<sup>1,2</sup>.

The present work considers in detail the effect of the dielectric constant of the reaction medium on the rate of hydrolysis of p-nitrophenyldiphenyl phosphate (NPDPP) in aqueous solutions containing the surfactant cetyltrimethylammonium bromide (CTAB) and various concentrations of sodium hydroxide and dimethyl sulfoxide (DMSO). Pseudo-first order ( $k_{\psi}$ ) and second order rate constants ( $k_2$ ) were measured at 15, 25 and 35°C using spectrophotometric techniques and activation parameters were also determined.

Some typical experimental results obtained for  $k_{\psi}$  at 25°C for solutions containing 0.01M NaOH and  $2.0 \times 10^{-3}$ M CTAB were:  $120.9 \times 10^{-3} \text{ sec}^{-1}$  (no DMSO);  $41.1 \times 10^{-3} \text{ sec}^{-1}$  (30% DMSO by volume) and  $170.1 \times 10^{-3} \text{ sec}^{-1}$  (90% DMSO by volume). For the solution without DMSO, the activation energy ( $E_a$ ) was 10.5 kcal.mol<sup>-1</sup>;  $\Delta S^{\ddagger}$  was -29.9 e.u. and  $\Delta G^{\ddagger}$  was 18.8 kcal.mol<sup>-1</sup>. The respective values for solutions containing 90% DMSO were 9.07 kcal.mol<sup>-1</sup>; -32.6 e.u. and 18.2 kcal.mol<sup>-1</sup>, respectively. The rate profiles obtained for solutions of CTAB-H<sub>2</sub>O-DMSO containing 10-50% DMSO showed clear maxima that shifted to higher concentrations of CTAB as a function of the DMSO added. For 60-80% DMSO there was no maximum rate and the reaction was inhibited. For the solutions containing 90% DMSO, the reaction rate was much higher evidencing the catalysis by DMSO.

In the absence of surfactant a linear relationship is obtained, between  $\log(k_{\psi})$  and the Lorentz function of the dielectric constants of the binary mixtures DMSO-H<sub>2</sub>O. When CTAB is added to the reaction medium there are two different situations. Beyond the formation of the hydrate DMSO.2H<sub>2</sub>O (>60% DMSO), that inhibits the CTAB micellization, the results are identical to those obtained in the systems with no surfactant. But in the presence of CTAB micelles, although we still obtain a linear relationship between  $\log(k_{\psi})$  and  $f(\epsilon)$ , this is quite different as compared to the other two cases. The same behaviour is found for the relationship between  $\log(k_{\psi})$  and a composite parameter calculated from the polarity and the donor number of the reaction media.

These results show, that a macroscopic property such as the dielectric constant of the medium may be used to describe the effect of DMSO on the hydrolysis rates both in the absence of surfactant or when this is dissolved as the monomer, but not in the presence of micellized surfactant.

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## **951.L1 USING OF TWO-PHASE AND THREE-PHASE MARKER FOAMS FOR DISCOVERING DAMAGED SECTIONS OF SUBSEA PIPELINE**

**Phung Dinh Thuc, Cariniou M.Ph., Tr.S. Phiet, Nguyen Phan Phuc, Nguyen Van Canh**  
*Vietsovpetro J. V.*

In the process of long-term operation on of subsea pipelines the natural aging occurs, that causes the damage and depressurizing. In this situation the correct and vast determination of the location of damage is very important not only because of admission decrease of oil and gas recovery or water injection, but also because environmental requirements. Detriment of environmental pollution can considerably excess the expenses, caused by change of field production condition. In this paper the experience of discovery of damaged sections of subsea pipeline at the depth of 50m by using marker foams is described. Foams were formed from solution of foam-form substances and air. In this method, the standard equipment of offshore fixed platform (air compressor and pump) were used. Liquid and solid substances were used as markers that is two-phase and three-phase foam were formed. The description of technology implementation as well as photographs of pipeline damaged section of water injection system are also given in this paper.

## **952.L1 EFFECTS OF QUINONES AND PHENOLS ON THE IMMOBILIZED BIOLUMINESCENT SYSTEM**

**Vetrova E.V., Hendogina E., Kudryasheva N.S.**  
*Institute of Biophysics, Krasnoyarsk, Russia*

The biotests are successfully used for the monitoring of the environmental pollutions. They show the rapid integral toxicity of ecology systems. Error of this method is 15-20%. The multicomponent immobilized luciferase reagent is suggested for the monitoring. It is based on the immobilized into the starch gel enzyme system NADH:FMN-oxidoreductase - bacterial luciferase. The starch films with immobilized components are in consistent with the requirements of the bioluminescent analytical sensors, i.e., the activity of important functional groups of the enzymes is preserved. The optimal microenvironment of bioluminescent enzymes were created, thus resulting in the increase of the efficiency of their work and stability. The goal of the present work was to investigate the possibility of use of the multicomponent immobilized reagent for monitoring of quinones and phenols in ecology systems. The effects of the rows of quinones and phenols on the immobilized enzyme bioluminescent system NADH:FMN-oxidoreductase-luciferase were studied. They were compared to these for the two other bioluminescent test-systems - luminescent bacteria and water soluble coupled enzyme bioluminescent system NADH:FMN-oxidoreductase - bacterial luciferase. The inhibition constants of intensity of bioluminescence (K) were calculated. The values of K were connected with the physical-chemical characteristics of the quinones and phenols. Electronic structure, different molecular weight, hydrophobic properties of the quinones and phenols were taken into account. It was stated that the immobilized test-system was less sensitive than water soluble one, and more sensitive than luminescent bacteria. These differences were connected with the various in structure of the test-systems: presence of the cell membrane, different diffusion rate of the substrates etc. In the presence of the quinones the immobilized test-system and the water soluble one were characterized by the induction period which depends on the quinone concentration. This makes the biotests specific for the group of quinones.

## **953.L1 STUDY ON DECOLOURING OF WASTEWATER OF PRINTWORKS BY COAL CINDER ADSORPTION**

**Luo Yatian, Fang Heping**  
*Dept. of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, P.R. China*

In this study the coal cinder was used to decolour the wastewater of printworks after biochemical treatment with good results. It was found that adsorption behaviour of the granular coal cinder was better than that of the powder coal cinder, which was the opposite adsorption behaviour between coal cinder and



activated carbon. The method of "treating waste with waste" is likely to become widely used in the future because the coal cinder is abundant and cheap, although the adsorptivity of the activated-carbon is much better than the coal cinder.

## 954.L2 DETERMINATION OF THE DYNAMIC SIZE OF A SMALL AGGREGATE

Lech Gmachowski

*Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland*

The most useful parameter for describing the dynamic behaviour of an airborne particle is its dynamic size. The dynamic radius  $r$  of a particle is the radius of an impermeable sphere of the same mass having the same dynamic properties. So, in the Stokes regime the steady-state falling speed of an aggregate composed of  $i$  spheres of radius  $a$ , normalized by the falling speed of the primary particle  $u_1$ , is described as:

$$\frac{u_i}{u_1} = \frac{r^2 (4/3)\pi a^3 i}{a^2 (4/3)\pi r^3} = \frac{i}{(r/a)} \Rightarrow \frac{r}{R} = \frac{i}{(R/a)(u_i/u_1)} \quad (1)$$

where the aggregate radius  $R$  is the radius of circumscribed sphere. The normalized hydrodynamic radius is also possible to calculate by the Brinkman equation for individual permeable sphere [1], using a reliable dependence of the dimensionless internal permeability  $k/R^2$  on the packing fraction  $\phi$ . Such a dependence has been recently verified [2] over a very wide concentration interval. Hence:

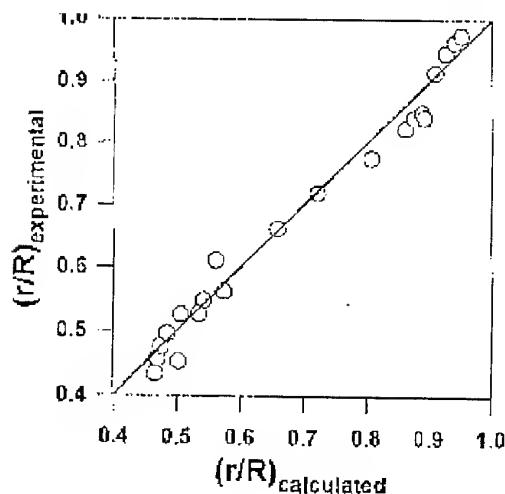
$$\left(\frac{r}{R}\right) = \frac{1 - \frac{\sqrt{k}}{R} \tanh \frac{R}{\sqrt{k}}}{1 + \frac{3}{2} \frac{k}{R^2} - \frac{3}{2} \frac{k\sqrt{k}}{R^3} \tanh \frac{R}{\sqrt{k}}}; \quad \frac{k}{R^2} = \frac{2}{9 \left(\frac{R}{a}\right)^2 \phi \left[1 + \frac{25\phi^{4/3}}{3(1-\phi)^3}\right]} \quad (2)$$

For some small aggregates the normalized hydrodynamic radii are possible to deduce from the experimental data [3,4] using Eq.(1). For comparison, they are calculated by Eq.(2). The presented figure shows the effectiveness of the proposed method.

The analyzed aggregates contain from 2 to 13 spheres including linear chains up to  $i=8$ , as well as compact aggregate of 13 spheres. If the aggregates begin to develop branched structure of spherical character, the dynamic radius is described by a universal function of the fractal dimension  $D$

$$\frac{r}{R} = \sqrt{1.56 - \left(1.728 - \frac{D}{2}\right)^2} - 0.228 \quad (3)$$

The applicability of this equation will be discussed [5].



1. H.C. Brinkman, *Proc. R. Dutch Acad. Sci.*, 50, 821 (1947)
2. L. Gmachowski, *J Chem.Engng Japan*, 29 (1996) (in press)
3. W. Stöber and H. Flachbart, *Environ. Sci. Technol.*, 3, 1280 (1969)
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5. L. Gmachowski, in preparation

## 955.L2

DETECTION OF SAHARAN AEROSOL OVER LAND  
WITH SATELLITE INFRARED MEASUREMENTSK. Ourtirane<sup>1</sup>, P. de Felice<sup>2</sup><sup>1</sup>University of Bejaia (Algeria),<sup>2</sup>L.M.D. Ecole Polytechnique de Palaiseau, France

Major dust storms can be produced over desert areas when there is sufficient wind to lift the particles above the surface. The aerosols can be over Sahara using the satellite data. During daytime, with clear conditions, desert land areas are strongly heated. Over the desert at midday, equivalent blackbody surface temperature, as measured in a 10,5 - 12,5  $\mu\text{m}$  atmospheric window, are often 15 - 20°K higher than the air temperature measured 1,2 m above the surface.

We use the notion of thermic contrast to locate the saharan aerosol and determine its direction. The zone which be considered is between the latitudes 20°N-50°N and the longitudes 15°W-15°E.

We consider six consecutive days having bad visibilities. The data of atmospheric radiances are obtained every three hours: 02h30, 05h30, 08h30, 11h30, 14h30, 17h30, 20h30 and 23h30.

We remark that the contrast between radiances of the land and aerosols is very high at 11h30 and 14h30. But at the night, the aerosol is heater than the land and the contrast is not very clear.

We trace the map of radiances and we calculate the horizontal moving speed of the aerosols. We remark that the aerosols move toward Atlantic and Europe.

## 956.L2

## OPTIC PROPERTIES OF AEROSOL LIFTED BY A BELLOWS

K. Ourtirane, R. Alkama, M. Cherchour

University of Bejaia (Algeria)

We simulate in laboratory a land subject to wind erosion. We use some instruments to lift the particles above the surface and to measure their optic properties. We measure the transmitted and scattered intensity at three spectral intervals (infrared, visible and UV) and at three heights: 0.20 m, 1 m, 2 m.

The sources which are used are: an infrared lamp (150W), and UV lamp (8W) and an incandescent lamp. The captors are: a photoresistance, a thermopile and a photoelectric cellule. The measures are done in presence and absence of aerosols.

The measure of horizontal extinctions for different lights and at three heights give the following results:

1. For the visible light: the extinction is equal to 17% at 20 cm. 12.85% at 1 m and 9.28% at 2 m.
2. For the infrared light: the extinction is equal to 12% at 1 m.
3. For the UV light: the extinction is equal to 5% at 1 m.

For the vertical transmission, the extinction is slighter. It is more important near the ground at visible and infrared light. The extinction coefficient is calculated by using the Beer-Lambert law.

957.L2 STUDY OF AMBIENT AIR POLLUTION WITH FIBROUS PARTICLES  
IN THE TOWN OF DIMITROVGRAD

Boriana Strokova, Savina Dimitrova

National Center of Hygiene, Medical Ecology and Nutrition, Sofia, Bulgaria

The problem about the carcinogenic effect of inhaled fibrous particles suspended in the air, mainly of asbestos, near to the towns with asbestos industry, is the object of numerous investigations all over the world during the last decades.

The object of former studies of air pollution with asbestos fibres in Bulgaria was working environment. On legal grounds (Decree No. 12 of the Ministry of Health, 1993) the use of asbestos-containing materials in living conditions is banned. Some kinds of them are permitted for application only in agriculture and stock-breeding.

The present research applies to airborne fibre pollution in Marinovo- suburban of Dimitrovgrad, where asbestos-cement roofing tiles are widely used for agricultural premises.

Samples were taken on October 2nd and 3rd, 1996. The sampling procedure followed the requirements of the Asbestos International Association Recommended Technical Method No. 2 (RTM 2). The fibre's counting and fibre's size distribution measurements were performed by transmission electron microscope "Hitachi" - HS-7S.

The results showed that asbestos fibres concentration with risk-related characteristics [length ( $l$ )  $\geq$  5 mm, diameter ( $d$ )  $<$  3 mm, aspect ratio ( $l:d$ )  $\geq$  3:1] exceeded many times the value of recommended safety level (0.001 fibres/cm<sup>3</sup>).

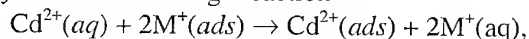
Asbestos emission investigations data from the industrial source - asbestos-cement factory "Vulkan" for the same period conformed with the permissible limit concentration. Based on the above-mentioned facts the authors conclude that the weathering of asbestos-cement roofing tiles could be considered as a potential source of asbestos fibres in urban ambient air. Extrasegregation of the tiles from the air, fibrous emissions control of ambient air and medical examinations of the population are recommended.

### 958.L3 THE TWO POPULATIONS OF ADSORPTION SITES ON KAOLINITE

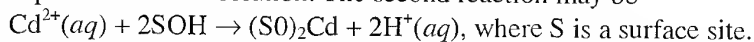
Michael J. Angove, Bruce B. Johnson and John D. Wells

*La Trobe University, Bendigo, Victoria 3552, Australia*

Cadmium(II) adsorbs to kaolinite by two distinct mechanisms(Angove et al., 1997). At low pH ( $<$  6) adsorption is exclusively by way of an ion exchange reaction



where  $\text{M}^{+}$  represents a cation (which may be  $\text{H}^{+}$ ) initially bound to a surface site. At higher pH ( $>$ 7) there is an additional reaction, in which Cd(II) forms bidentate inner-sphere complexes with surface hydroxyl groups, with the simultaneous release of protons into the solution. The second reaction may be



Evidence for these processes comes from three independent sets of data: adsorption edges, in which the amount of Cd(II) lost from an initial solution is measured as the pH is raised in steps from about 3 to 10; adsorption isotherms, where the adsorption of Cd<sup>II</sup> at constant pH is measured over a range of concentrations; and surface charge titrations, in which a suspension of kaolinite is titrated with base, with or without added cadmium.

We have been able to model all of these data with a self-consistent set of parameters, but only if we allow for the two distinct processes set out above. The parameters we obtain are consistent with the hypothesis that the ion exchange reaction takes place on the permanently charged sites of the siloxane surface, and the direct adsorption process occurs on the variable charge aluminol sites.

Our earlier work (Angove et al., 1997) was at 25°C. This paper reports the results of experiments at several other temperatures from 10°C to 70°C, which further support the two-site hypothesis. We have also conducted a parallel study of the adsorption of cobalt (II) onto kaolinite over a range of pH, concentration and temperature.

M. J. Angove, B. B. Johnson, and J. D. Wells (1997) *Colloids Surfaces* (in the press).

### 959.L3 INFLUENCES OF SEVERAL SOIL COLLOIDS IN CENTRAL-SOUTH CHINA ON THE ADSORPTION AND PROPERTIES OF UREASE ENZYME

Huang Qiaoyun, Jiang Minghua, Yang Zhijian and Li Xueyuan

*Department of Natural Resources and Environmental Science,  
Huazhong Agricultural University Wuhan, P.R. China*

Soil colloid is the finest and the most active solid component in soils. By the association with soil enzymes which are important indices of soil fertility and quality, soil colloid exerts profound influences on a variety of enzyme characteristics. Today, soil and agricultural scientists have paid more and more attention to the exploitation, protection and management of the soils in tropical and subtropical areas which is

currently the key regions for agricultural development. However, prior to this study, very little information is available with regard to the interactions between the colloids of the above-mentioned soils and enzymes. The present experiment, therefore was designed to elucidate the effects of the sterilized colloids separated from red soil, latosol and yellow brown soil which are the typical zonal soils in central-south China, on the adsorption, activity, kinetic parameters and thermal-stability of urease enzyme which plays significant role in the transformation of soil nitrogen compounds. Results showed that the amount of enzyme adsorbed in the examined soil colloids followed the order: yellow brown soil > red soil  $\approx$  latosol. The residual activities of enzyme in different colloid systems were in the following sequence: red soil > latosol > yellow brown soil. The thermal stability of adsorbed enzyme was higher than that of free enzyme. The enzyme immobilized on yellow brown soil colloid had the highest stability at elevated temperature from 60°C to 80°C. Both the free and the immobilized urease obeyed Michaelis-Menten kinetics. The  $K_m$  values of immobilized urease (13.5-20.8 mM) on different soil colloids examined were in the same order of magnitude as that of free urease (g. 3 mM). The kinetic constant of immobilized enzyme suggested that urease adsorbed on yellow brown soil colloid had a greater affinity for substrate. The  $K_m$  and  $V_{max}$  values also indicated a mixed type of enzyme inhibition for the examined soil colloids. These results provided basic evidences for the understanding of the properties and kinetics of soil enzymes in tropic and subtropic regions.

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Poltoratsky, G. 518.E2  
Polunina, I.A. **521.E2** **623.E5**  
Polyakova, Y.V. 575.E4  
Pomonis, P.J. 106.A5  
Pompe, W. 169.B2  
Poncelet, D. 637.F1  
Ponsinet, V. **225.B4** **383.D1**  
Popov, A. **664.F1**  
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Popovskiy, A.Yu. **150.B2**  
Popovskiy, Yu.M. **150.B2**  
Poptoshev, E. **163.B2**  
Porodenko, E.V. **046.A3**  
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Potesnova, M.V. **947.L1**  
Poulligny, B. 417.D3  
Pravdic, V. 949.L1  
Pravdin, V.G. **850.H3**  
Prestidge, C. 007.A1  
Prieve, D.C. **660.F1**  
Princen, H.M. **226.B4**  
Prins, A. 049.A3 **738.G1**  
Pritykin, L.M. **583.E4**  
Proust, J.E. 555.E4 570.E4 **584.E4** 723.G1  
725.G1 863.H4  
Prüger, B. 716.F3 718.F3 721.F3  
Prunet-Foch, B. 236.B4  
Pruska-Kedzior, A. 894.K2  
Psarrou, S. 644.F1  
Puccetti, G. 183.B3  
Pugh, R.J. 163.B2  
Pum, D. 826.H1  
Putilin, A.F. **128.A6**  
Putman, B. **670.F1**  
Pychteeva, E.G. 101.A5  
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Rabinovich, Y.I. **027.A2**  
Racz, G. 047.A3

Radeva, Ts.	703.F2	704.F2			Rynda, Y.F.	547.E3			
Radke, C.J.	592.E4	319.C1	168.B2	233.B4	Saarinен, T.	629.E5			
	491.E1				Sackmann, E.	415.D3	831.H1		
Radoev, B.	VI.	133.B1	160.B2	177.B3	Sadykov, V.	899.K3			
	181.B3	333.C2	742.G1	776.G3	Saenger, W.	111.A6			
Rager, T.	384.D1				Safi, O.	545.E3			
Raicevic, S.	948.L1				Sageant, D.L.	440.D4			
Raiteri, R.	308.C1				Saidi, H.	706.F2			
Rajagopalan, R.	027.A2				Saidi, N.	706.F2			
Rakshit, A.K.	624.E5				Saidov, A.A.	359.D1	398.D2	429.D4	700.F2
Ralston, J.	007.A1	108.A6	262.B5	573.E4	Saint, N.	827.H1			
	908.K4	910.K4	911.K4		Sakai, H.	261.B5			
					Sakakibara, T.	677.F1			
Ramos de Souza, E.	164.B2				Sakhypov, F.	899.K3			
Ramos, L.	385.D1				Salah, D.	449.D5			
Ramos-Barrado, J.R.	687.F1	688.F1			Samsonov, V.M.	229.B4	230.B4		
Rana, F.	386.D1				Sanders, R.S.	902.K3			
Rangaraj, A.	624.E5				Sanderson, N.M.	879.H5			
Ranieri, G.A.	360.D1				Sandor, N.	047.A3			
Rankin, A.	243.B5				Sano, Y.	370.D1			
Ransac, S.	822.H1				Sarac, A.	625.E5			
Rao, R.	486.E1				Saramago, B.J.V.	201.B4	854.H3		
Rapp, G.	369.D1	464.E1	465.E1	804.H1	Sasaki, S.	450.D5			
	811.H1	821.H1	880.H5		Sato, K.	276.B6			
Rasmusson, M.	671.F1				Sato, N.	264.B5	396.D1		
Rasulova, G.E.	934.L1				Saulnier, P.	676.F1	863.H4		
Raudino, A.	724.G1				Saunders, B.R.	126.A6			
Ravera, F.	463.E1	731.G1	732.G1	739.G1	Sautter, E.	559.E4			
Razilov, I.A.	715.F3				Saville, D.A.	685.F1			
Real Oliveira, M.E.C.D.	437.D4				Savina, I.	526.E2			
Rebouillat, S.	260.B5				Savitskaya, A.N.	006.A1			
Rees, G.D.	438.D4				Scarpelli, E.M.	871.H4			
Regev, O.	412.D3	447.D5			Schagina, L.V.	810.H1			
Rehmet, R.	557.E4				Schalke, M.	826.H1			
Reiners, J.	240.B4				Schaub, M.	402.D2			
Reinhoudt, D.N.	123.A6				Schiller, P.	190.B3	387.D1		
Remisov, G.P.	301.C1				Schlacken, H.	190.B3			
Remizov, S.V.	777.G3				Schmidt, F.	522.E2			
Rennie, A.R.	507.E2				Schmidt, C.	778.G3			
Retter, U.	672.F1	673.F1			Schmitt, F.-J.	586.E4			
Rheinländer, T.	098.A5	891.K1			Schneemilch, M.	262.B5			
Rich, G.T.	851.H3				Schoeman, B.J.	099.A5			
Richter, L.	240.B4	330.C2			Schönherr, H.	402.D2			
Riede, A.	127.A6				Schönhoff, M.	523.E2			
Riegler, H.	227.B4	228.B4			Schudel, M.	281.C1			
Rigby, G.	274.B6				Schulz, J.	524.E2			
Riley, T.	881.H5				Schulze, H.J.	216.B4	266.B5	333.C2	742.G1
Ringsdorf, H.	402.D2				Schürch, S.	852.H3			
Riviere, C.	812.H1				Schurtenberger, P.	281.C1			
Robillard, B.	853.H3				Schwuger, M.J.	525.E2			
Robins, M.	769.G3				Sedev, R.	290.C1	306.C1	309.C1	325.C2
Robinson, A.M.	879.H5					339.C2	344.C2	587.E4	765.G3
Robinson, B.H.	438.D4	440.D4				872.H4			
Rodenas, E.	460.E1	461.E1			Seguer, J.B.	370.D1			
Rodicheva, E.K.	835.H2				Seidel, O.	190.B3	364.D1	387.D1	449.D5
Rodin, V.	899.K3					779.G3			
Rodin, V.V.	067.A4	870.H4			Selyutin, O.B.	583.E4			
Rogueda, P.G.A.	504.E2				Semal, S.	263.B5			
Roldughin, V.I.	125.A6	144.B1			Semashko, O.	345.C2			
Rondelez, F.	826.H1				Semmler, M.	281.C1			
Roques, B.P.	389.D1				Semmler, W.	098.A5			
Rosa, M.E.	165.B2				Senée, J.	853.H3			
Rösch, L.	760.G3				Serebryakova, N.V.	100.A5	529.E2		
Rosenbusch, J.P.	827.H1				Serro, A.P.	854.H3			
Rosenholm, J.B.	353.C3				Setzer, M.J.	175.B3			
Roser, J.	581.E4				Severianova, M.A.	790.G4	843.H3		
Roshchina, T.M.	585.E4				Shabarchina, L.I.	856.H3			
Rotstegge, J.	028.A2				Shah, S.S.	487.E1			
Rovillard, S.	239.B4	661.F1	674.F1		Shanahan, M.E.R.	203.B4	740.G1	794.G4	
Rowlands, W.	671.F1				Shapir, Y.	729.G1			
Rozhkov, A.	001.A1	031.A3			Shapiro, Yu.E.	101.A5	855.H3		
Ruckenstein, E.	068.A4				Sharaf, A.	001.A1			
Rudakova, E.	705.F2				Sharma, A.	166.B2			
Rudnitsky, L.A.	675.F1				Shau, F.S.	135.B1			
Rugg-gunn, A.J.	862.H4				Shchekin, A.K.	277.B6	278.B6		
Rusanov, A.I.	145.B1	278.B6			Shcherbakov, L.M.	229.B4			
Rutland, M.	321.C2				Shchipunov, Yu.A.	451.D5	741.G1		
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**Shenkov, S.** 626.E5 888.K1  
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**Shramko, O.** 679.F1 707.F2  
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**Shubin, V.** 588.E4  
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**Simakova, G.A.** 069.A4  
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**Simon, F.** 678.F1 636.F1  
**Simonova, T.** 679.F1 680.F1 681.F1 707.F2  
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 Snctanina, I.E. 029.A2  
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**Smirnova, N.P.** 102.A5  
**Smorodin, V.Ye.** 114.A6 231.B4 310.C1 818.H1  
**Soares, B.G.** 582.E4  
**Soholev, V.D.** 153.B2 213.B4  
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**Sprycha, R.** 617.E5  
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**Stoimenova, M.** 708.F2 709.F2  
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**Stoylov, S.P.** 389.D1 453.D5 655.F1 706.F2  
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**Szczypa, J.** 683.F1  
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**Szymanowski, J.** 457.E1 497.E2 498.E2 923.K4  
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**Tadmor, R.** 297.C1 312.C1  
**Tadros, Th.F.** 527.E2 881.H5  
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**Tajima, K.** 072.A4 192.B3 390.D1  
**Takagi, R.** 684.F1  
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**Tanaka, M.** 379.D1 492.E1  
**Tanaka, R.** 441.D4  
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| Tazhibaeva, S.M.   | 620.E5 |        |        |        | Um, S.-U.              | 163.B2 |        |               |
| Tchesskaya, T.Yu.  | 546.E3 |        |        |        | Umbach, P.             | 111.A6 |        |               |
| Teeter, J.H.       | 810.H1 |        |        |        | Umesawa, M.            | 092.A5 |        |               |
| Teixeira, A.V.     | 118.A6 |        |        |        | Ung, T.                | 091.A5 |        |               |
| Telegin, G.G.      | 694.F2 |        |        |        | Uryupina, O.Ya.        | 529.E2 |        |               |
| Temnikova, S.V.    | 605.E5 |        |        |        | Us'yarov, O.           | 314.C1 | 345.C2 |               |
| Tenchoy, B.        | 342.C2 | 355.D1 | 405.D3 | 811.H1 | Usui, Y.               | 086.A5 |        |               |
|                    | 821.H1 | 823.H1 | 880.H5 |        | Vakarelsky, I.U.       | 743.G1 |        |               |
| ter Horst, J.H.    | 593.E4 |        |        |        | Valiente, M.           | 460.E1 | 461.E1 |               |
| Terenzi, M.        | 360.D1 |        |        |        | Valignat, M.P.         | 152.B2 | 170.B2 | 239.B4        |
| Terry, A.          | 381.D1 |        |        |        | van Aken, G.A.         | 049.A3 |        |               |
| Tertykh, L.I.      | 547.E3 |        |        |        | van de Ven, T.G.M.     | 903.K3 |        |               |
| Terziev, L.        | 644.F1 | 657.F1 |        |        | van der Leeden, M.C.   | 544.E3 |        |               |
| Terzieva, V.       | 644.F1 |        |        |        | van der Linde, R.      | 237.B4 | 238.B4 |               |
| Testard, F.        | 442.D4 |        |        |        | Van der Meeren, P.     | 670.F1 | 896.K2 |               |
| Testov, V.G.       | 050.A3 |        |        |        | van der Zande, B.M.I.  | 105.A5 |        |               |
| Theodorou, D.N.    | 319.C1 |        |        |        | van Duynhoven, J.P.M.  | 123.A6 |        |               |
| Thiele, U.         | 169.B2 |        |        |        | van Herk, A.M.         | 411.D3 |        |               |
| Thomas, J.C.       | 108.A6 |        |        |        | van Kalsbeek, H.K.A.I. | 049.A3 |        |               |
| Thomas, R.K.       | 507.E2 |        |        |        | van Maris, R.          | 047.A3 |        |               |
| Thompsen, L.       | 563.E4 |        |        |        | van Opheusden, J.H.J.  | 109.A6 |        |               |
| Thuc, P.D.         | 951.L1 |        |        |        | van Rosmalen, G.M.     | 593.E4 |        |               |
| Thuresson, K.      | 11.    |        |        |        | van Vreeswijk, J.      | 630.E5 |        |               |
| Tian, J.           | 256.B5 |        |        |        | Vanderdeelen, J.       | 896.K2 |        |               |
| Tiberg, F.         | 11.    |        |        |        | Vargha-Butler, E.I.    | 882.H5 |        |               |
| Tiddy, G.J.T.      | V.     | 361.D1 | 368.D1 | 381.D1 | Varzhel, V.I.          | 693.F1 |        |               |
|                    | 386.D1 |        |        |        | Vasilescu, M.          | 631.E5 |        |               |
| Tieck, B.          | 606.E5 | 607.E5 |        |        | Vasiliev, E.I.         | 050.A3 |        |               |
| Tien, H.T.         | 391.D1 | 815.H1 |        |        | Vassilieff, C.S.       | 413.D3 | 767.G3 | 797.G4        |
| Timmerman, A.      | 528.E2 |        |        |        | Vasyutkin, N.F.        | 197.B3 |        |               |
| Timofeev, V.P.     | 397.D1 |        |        |        | Vdovic, N.             | 949.L1 |        |               |
| Timoshic, M.S.     | 585.E4 |        |        |        | Velazquez, P.          | 687.F1 | 688.F1 |               |
| Titeva, St.        | 770.G3 |        |        |        | Velev, O.D.            | 018.A1 | 171.B2 | 172.B2        |
| Toca-Herrera, J.L. | 348.C2 |        |        |        | Velikov, K.P.          | 171.B2 | 172.B2 | 417.D3        |
| Todorov, R.K.      | 283.C1 | 711.F2 | 864.H4 | 869.H4 | Velitchkova, M.        | 801.H1 |        |               |
| Toledano, O.       | 858.H3 |        |        |        | Velizarov, S.          | 932.L1 |        |               |
| Tolstorukov, M.Ye. | 403.D2 |        |        |        | Verclas, S.A.W.        | 825.H1 |        |               |
| Tomimitsu, T.      | 509.E2 |        |        |        | Verger, R.             | 570.E4 | 584.E4 | 807.H1 808.H1 |
| Tonova, K.         | 474.E1 |        |        |        |                        | 812.H1 | 822.H1 |               |
| Topchieva, I.N.    | 392.D1 |        |        |        | Versmold, H.           | 734.G1 |        |               |
| Toshev, B.V.       | VI.    | 133.B1 | 270.B6 |        | Vetrova, E.V.          | 952.L1 |        |               |
| Tóth-Boconádi      | 820.H1 |        |        |        | Vignes-Adler, M.       | 156.B2 | 236.B4 | 853.H3        |
| Tournilhac, F.     | 567.E4 |        |        |        | Viken, E.              | 255.B5 |        |               |
| Tovbin, Yu.K.      | 196.B3 | 197.B3 |        |        | Vikhoreva, G.A.        | 599.E5 |        |               |
| Toyomasu, T.       | 176.B3 |        |        |        | Vila Romeu, N.         | 494.E1 |        |               |
| Trahms, L.         | 891.K1 |        |        |        | Vila, A.O.             | 394.D1 |        |               |
| Tran, D.           | 255.B5 |        |        |        | Vilkova, N.G.          | 039.A3 |        |               |
| Trau, M.           | 393.D1 | 685.F1 |        |        | Villeneuve, M.         | 530.E2 |        |               |
| Trejo, L.M.        | 048.A3 | 146.B1 |        |        | Villette, S.           | 239.B4 |        |               |
| Troian, S.S.       | 207.B4 |        |        |        | Vincent, B.            | 126.A6 | 315.C1 |               |
| Trusov, A.A.       | 689.F1 | 705.F2 |        |        | Vinetsky, Y.           | 632.E5 |        |               |
| Tsai, J.-S.        | 892.K2 |        |        |        | Vinogradova, O.I.      | 316.C1 |        |               |
| Tsakova, V.        | 591.E4 |        |        |        | Virnik, K.M.           | 403.D2 |        |               |
| Tsarkova, L.A.     | 924.K4 |        |        |        | Viseu, M.I.            | 418.D3 | 757.G2 |               |
| Tsckov, R.         | 160.B2 | 406.D3 | 413.D3 | 742.G1 | Vishnyakov, A.         | 147.B1 |        |               |
| Tsekova, D.        | 859.H3 |        |        |        | Visschers, M.          | 237.B4 | 238.B4 |               |
| Tseng, M.-T.       | 295.C1 |        |        |        | Vivek, S.              | 317.C1 |        |               |
| Tsiourvas, D.      | 103.A5 |        |        |        | Vladikova, D.          | 682.F1 |        |               |
| Tsoneva, I.        | 322.C2 |        |        |        | Vladkova, R.           | 823.H1 |        |               |
| Tsuchida, A.       | 701.F2 |        |        |        | Vladkova, T.           | 873.H4 |        |               |
| Tsujii, K.         | 264.B5 | 396.D1 |        |        | Vlahovska, P.M.        | 743.G1 | 744.G1 |               |
| Tsukada, M.        | 844.H3 |        |        |        | Voelkel, A.            | 457.E1 |        |               |
| Tukhbatullin, F.   | 899.K3 |        |        |        | Vogt, S.               | 581.E4 |        |               |
| Tuncay, M.         | 493.E1 |        |        |        | Voicu, A.              | 458.E1 |        |               |
| Tuparev, N.        | 686.F1 |        |        |        | Voitylov, V.V.         | 689.F1 |        |               |
| Tupy, M.J.         | 592.E4 |        |        |        | Volchkova, I.L.        | 120.A6 | 128.A6 | 777.G3        |
| Turi, I.           | 079.A5 |        |        |        | Vollhardt, D.          | 198.B3 |        |               |
| Tursunov, Sh.O.    | 429.D4 |        |        |        | Voloshin, A.G.         | 697.F2 |        |               |
| Tusa, A.           | 215.B4 |        |        |        | Voué, M.               | 239.B4 | 244.B5 | 263.B5        |
| Tusupbaev, N.K.    | 313.C1 |        |        |        | Voznjakovsky, A.P.     | 074.A5 |        |               |
| Tutorsky, I.A.     | 069.A4 |        |        |        | Vuillenmier, C.        | 389.D1 |        |               |
| Tvarozek, V.       | 815.H1 |        |        |        | Vyazmin, A.V.          | 798.G4 |        |               |
| Tzong-Fuu, C.      | 061.A4 |        |        |        | Vybornova, L.A.        | 691.F1 |        |               |
| Ueda, I.           | 874.H4 |        |        |        | Vysotsky, V.V.         | 125.A6 |        |               |
| Ueno, S.           | 276.B6 |        |        |        | Wachtel, E.            | 424.D4 |        |               |
| Uhomoibhi, J.      | 033.A3 |        |        |        | Wagner, R.             | 240.B4 |        |               |
| Ullah, H.          | 487.E1 |        |        |        | Wagner, T.M.           | 915.K4 |        |               |



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|----------------------|--------|--------|--------|--------|
| Wahab, M.            | 364.D1 | 387.D1 |        |        |
| Wakabayashi, H.      | 887.K1 |        |        |        |
| Walde, P.            | 414.D3 | 824.H1 |        |        |
| Walderhaug, H.       | 633.E5 |        |        |        |
| Wall, S.             | 129.A6 | 635.F1 |        |        |
| Walldal, C.          | 129.A6 |        |        |        |
| Walstra, P.          | 109.A6 |        |        |        |
| Wan, H.              | 909.K4 |        |        |        |
| Wang, J.             | 799.G4 |        |        |        |
| Wang, R.             | 745.G1 |        |        |        |
| Wanles, E.J.         | 365.D1 | 395.D1 | 531.E2 |        |
| Wantke, K.-D.        | 043.A3 | 051.A3 | 781.G3 |        |
| Warne, B.            | 081.A5 |        |        |        |
| Warshavsky, V.B.     | 277.B6 |        |        |        |
| Warszynski, P.       | 035.A3 | 496.E2 | 532.E2 |        |
| Wasan, D.T.          | 221.B4 | 292.C1 | 318.C1 |        |
| Wasserman, A.M.      | 397.D1 |        |        |        |
| Waton, G.            | 376.D1 |        |        |        |
| Watson, A.           | 769.G3 |        |        |        |
| Weaire, D.           | 045.A3 | 052.A3 |        |        |
| Wegner, G.           | 384.D1 |        |        |        |
| Weidenhammer, P.     | 586.E4 |        |        |        |
| Weis, J.             | 578.E4 | 760.G3 |        |        |
| Weissman, J.M.       | 452.D5 |        |        |        |
| Weissmüller, J.      | 240.B4 |        |        |        |
| Weitschies, W.       | 098.A5 | 891.K1 |        |        |
| Wells, J.D.          | 914.K4 | 958.L3 |        |        |
| Welsh, G.            | 440.D4 |        |        |        |
| Welters, W.J.J.      | 267.B5 |        |        |        |
| Wen, Z.              | 055.A4 |        |        |        |
| Wennerström, H.      | 065.A4 |        |        |        |
| Wesley, R.           | 563.E4 |        |        |        |
| Wetzer, B.           | 826.H1 |        |        |        |
| Weygand, M.          | 506.E2 | 825.H1 | 826.H1 |        |
| Wick, R.             | 824.H1 |        |        |        |
| Widmaier, J.         | 130.A6 |        |        |        |
| Wiese, H.            | 119.A6 |        |        |        |
| Wilde, P.J.          | 893.K2 |        |        |        |
| Wilhelm, M.          | 028.A2 | 063.A4 |        |        |
| Wilk, K.A.           | 374.D1 | 439.D4 |        |        |
| Williams, C.E.       | 545.E3 |        |        |        |
| Williams, P.M.       | 019.A2 |        |        |        |
| Wilson, J.           | 381.D1 |        |        |        |
| Winnik, F.M.         | 537.E3 |        |        |        |
| Winter, S.J.         | 319.C1 |        |        |        |
| Winterhalter, M.     | 334.C2 | 409.D3 | 827.H1 |        |
| Witkamp, G.J.        | 593.E4 |        |        |        |
| Wójcik, W.           | 241.B4 |        |        |        |
| Wolf, H.             | 402.D2 |        |        |        |
| Wolszczak, M.        | 483.E1 |        |        |        |
| Wong Fong Sang, K.E. | 593.E4 |        |        |        |
| Wu, X.               | 763.G3 | 903.K3 | 913.K4 |        |
| Wu, Y.               | 240.B4 |        |        |        |
| Wüstneck, R.         | 517.E2 | 619.E5 |        |        |
| Wyn-Jones, E.        | 368.D1 | 609.E5 |        |        |
| Wyrwas, B.           | 942.L1 | 943.L1 | 944.L1 |        |
| Xenakis, A.          | 420.D4 |        |        |        |
| Xiang, G.K.          | 882.H5 |        |        |        |
| Xiaoping, B.         | 253.B5 |        |        |        |
| Xiong, C.D.          | 881.H5 |        |        |        |
| Xiuping, S.          | 925.K4 |        |        |        |
| Yakovenko, T.M.      | 278.B6 |        |        |        |
| Yakubov, G.          | 233.B4 |        |        |        |
| Yamamoto, H.         | 860.H3 |        |        |        |
| Yamamoto, K.         | 191.B3 |        |        |        |
| Yamamoto, T.         | 396.D1 |        |        |        |
| Yamanaka, M.         | 874.H4 | 868.H4 |        |        |
| Yamanaka, T.         | 282.C1 | 323.C2 | 349.C2 |        |
| Yamaoka, K.          | 712.F2 |        |        |        |
| Yaminsky, V.V.       | 320.C1 |        |        |        |
| Yampolskaya, G.P.    | 034.A3 | 173.B2 |        |        |
| Yan, W.-J.           | 135.B1 |        |        |        |
| Yanata, A.           | 194.B3 |        |        |        |
| Yang, C.             | 690.F1 |        |        |        |
| Yang, P.             | 596.E4 |        |        |        |
| Yang, Z.             | 959.L3 |        |        |        |
| Yanishlieva, N.V.    | 085.A5 |        |        |        |
| Yankov, R.           | 036.A3 | 290.C1 | 300.C1 | 343.C2 |
| Yano, J.             | 276.B6 |        |        |        |
| Yao, A.              | 788.G4 |        |        |        |
| Yapar, S.            | 533.E2 |        |        |        |
| Yaremko, Z.M.        | 580.E4 | 780.G3 |        |        |
| Yaroshenko, N.A.     | 495.E1 | 520.E2 | 534.E2 |        |
| Yaroslavov, A.A.     | 594.E4 | 627.E5 | 828.H1 |        |
| Yaroslavova, E.G.    | 594.E4 |        |        |        |
| Yatian, L.           | 953.L1 |        |        |        |
| Yemelyanov, D.N.     | 029.A2 | 595.E4 | 782.G3 |        |
| Yeremenko, S.I.      | 115.A6 | 445.D5 |        |        |
| Yildirim, H.         | 625.E5 |        |        |        |
| Yonezawa, T.         | 350.C2 |        |        |        |
| Yongjian, L.         | 926.K4 |        |        |        |
| Yoon, R.-H.          | 174.B2 | 317.C1 | 922.K4 |        |
| Yoshida, M.          | 092.A5 |        |        |        |
| Yoshida, T.          | 834.H2 |        |        |        |
| Yoshikawa, H.        | 890.K1 |        |        |        |
| Yoshikawa, Y.        | 720.F3 |        |        |        |
| Yoshimoto, T.        | 182.D3 |        |        |        |
| Yoshino, S.          | 746.G1 |        |        |        |
| Yuan, H.             | 815.H1 |        |        |        |
| Yuan, J.             | 245.B5 | 907.K4 |        |        |
| Yuasa, R.            | 842.H3 |        |        |        |
| Yüce, N.             | 493.E1 |        |        |        |
| Yui, T.T.            | 783.G3 |        |        |        |
| Yuqing, L.           | 904.K3 |        |        |        |
| Yurkova, I.N.        | 841.H3 | 927.K4 |        |        |
| Zadymova, N.M.       | 073.A4 | 480.E1 | 481.E1 | 535.E2 |
|                      | 947.L1 |        |        |        |
| Zagaytov, A.I.       | 548.E3 |        |        |        |
| Zaitsev, S.Yu.       | 599.E5 |        |        |        |
| Zaitsev, V.N.        | 259.B5 |        |        |        |
| Zajkov, O.           | 829.H1 |        |        |        |
| Zakharov, A.V.       | 148.B1 |        |        |        |
| Zakharov, V.V.       | 149.B1 |        |        |        |
| Zakharova, J.A.      | 397.D1 |        |        |        |
| Zakin, J.L.          | 476.E1 |        |        |        |
| Zakordonskiy, V.P.   | 780.G3 |        |        |        |
| Zaman, A.            | 027.A2 |        |        |        |
| Zana, R.             | 376.D1 |        |        |        |
| Zaniquelli, M.E.D.   | 468.E1 |        |        |        |
| Zao, S.              | 199.B3 |        |        |        |
| Zarlaha, A.D.        | 106.A5 |        |        |        |
| Zastrow, H.          | 590.E4 |        |        |        |
| Zatovsky, A.V.       | 546.E3 |        |        |        |
| Zdravomislov, M.V.   | 132.B1 |        |        |        |
| Zechen, O.           | 926.K4 |        |        |        |
| Zeltonozskaya, T.B.  | 564.E4 |        |        |        |
| Zemb, Th.            | 442.D4 | 446.D5 |        |        |
| Zernova, T.Yu.       | 689.F1 |        |        |        |
| Zhang, G.            | 268.B5 | 269.B5 |        |        |
| Zhang, T.            | 596.E4 |        |        |        |
| Zhang, W.            | 199.B3 | 788.G4 |        |        |
| Zharkich, N.I.       | 634.F1 |        |        |        |
| Zharov, A.I.         | 116.A6 |        |        |        |
| Zheliaskova, A.      | 404.D2 |        |        |        |
| Zhendong, S.         | 928.K4 |        |        |        |
| Zheng, Y.            | 476.E1 |        |        |        |
| Zhilentkov, E.L.     | 691.F1 |        |        |        |
| Zhivkov, A.M.        | 453.D5 | 549.E3 | 713.F2 | 830.H1 |
| Zhivkova, I.V.       | 549.E3 |        |        |        |
| Zhou, T.-A.          | 815.H1 |        |        |        |
| Zhu, Y.              | 268.B5 | 269.B5 | 918.K4 |        |
| Zhukov, A.N.         | 692.F1 | 693.F1 |        |        |
| Zhuoming, G.         | 200.B3 |        |        |        |
| Zinoviev, V.V.       | 800.G4 |        |        |        |
| Zitha, P.            | 550.E3 |        |        |        |
| Zobel, G.            | 232.B4 |        |        |        |
| Zolotarev, P.P.      | 551.E3 |        |        |        |
| Zongqi, C.           | 428.D4 |        |        |        |
| Zorin, Z.            | 345.C2 |        |        |        |
| Zubarev, A.Y.        | 009.A1 |        |        |        |
| Zubov, V.P.          | 599.E5 |        |        |        |
| Zutic, I.            | 755.G2 |        |        |        |
| Zutic, V.            | 296.C1 | 654.F1 | 749.G2 | 857.H3 |
| Zwierzukowski, W.    | 071.A4 | 536.E2 |        |        |